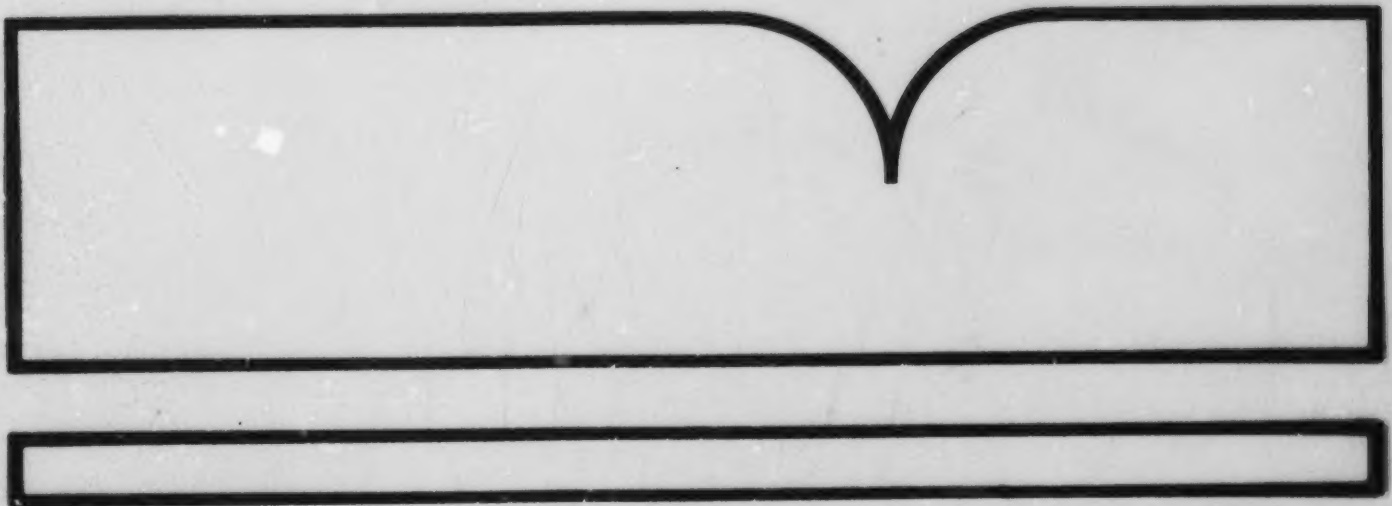


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Miniature Acid Condensation System
Design and Operation

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Research Triangle Park, NC

Apr 84



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April 1984

MINIATURE ACID CONDENSATION SYSTEM
Design and Operation

by

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ABSTRACT

An extractive source sampling system was designed and constructed. The sampling system measures gaseous sulfuric acid and sulfur dioxide in combustion emissions. The miniature acid condensation system (MACS) includes a high-temperature quartz probe and quartz-filter holder. The temperatures of the probe and filter are maintained at or above 520°F during sampling with temperature controllers. After removal of particles from the source sample with a flat quartz filter, the sulfuric acid is collected in a glass-wool plug. The glass-plug temperature is maintained at 140°F with a water bath circulator. Subsequent midjet impingers containing hydrogen peroxide collect sulfur dioxide.

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SECTION 1

INTRODUCTION

The initial purpose for measuring the presence of sulfuric acid (H_2SO_4) in combustion emissions was to prevent corrosion. Pioneering work in this area by Taylor¹, Johnstone², and Goksoyr³ addressed either extractive sampling methods for such measurements or in situ measurement of the H_2SO_4 dew point. The difficulty with measuring H_2SO_4 (commonly termed SO_3 in older literature citations) is the possible interference which results from sulfur dioxide (SO_2) oxidation.⁴ Because of this problem, the preferred method in the earlier works was the selective temperature-controlled condensation of H_2SO_4 which separated SO_2 from the acid by maintaining SO_2 in the gas phase. Subsequent collection of the SO_2 in hydrogen peroxide (H_2O_2) solutions provided a measure of the residual sulfur oxide.

More recent efforts to measure H_2SO_4 in combustion systems are related to increases in the amount of residual high-sulfur fuel oil use, and in the attention given to environmental impact. As a result of this increased attention, methods were re-evaluated for precision and reliability. The general consensus from this evaluation confirmed the temperature-controlled condensation of H_2SO_4 as the preferred method for such measurements.⁵ Thus, developments in methodology have focused on the precision of the method, optimum design for extractive sampling systems, and the establishment of prescribed procedures⁶ for such methods.

Several sampling-system designs which address H_2SO_4 collection efficiency and SO_2 interference have been evaluated^{7,8,9}. As prototype

systems and procedures were refined, a practical "low-effort," easily handled, and reliable sampling system evolved.

Currently, a system for H_2SO_4 sampling is not commercially available; however, there appears to be continued interest in performing these measurements. The purpose of this work is to provide some guidance for the fabrication of an easily operated and highly portable gaseous H_2SO_4 sampling system.

SECTION 2

SYSTEM DESCRIPTION

REVIEW OF SYSTEM

Figure 1 presents a functional diagram of the miniature acid-condensation sampling system (MACS). The basic components of the system are the heated quartz sample probe, filter holder, electrical temperature control unit, water-jacketed glass-plug holder, constant-temperature water bath, impinger train/ice bath container, and sample pump unit. Section 4 of this report gives specifications and detailed drawings for each component.

Heated Quartz Sample Probe

The heated quartz sample probe (Figure 2) is composed of a quartz tube equipped with heating tape, stack and probe temperature sensors, and a 2.54 cm (1 in.) stainless-steel sheathing.

Quartz-filter Holder

The quartz-filter holder (Figure 3) is a slightly modified 28/15 quartz joint equipped with a coarse-frit-filter support, a temperature sensor, and a heating mantle. During operation a 16-mm-diameter high purity quartz filter is positioned in the holder.

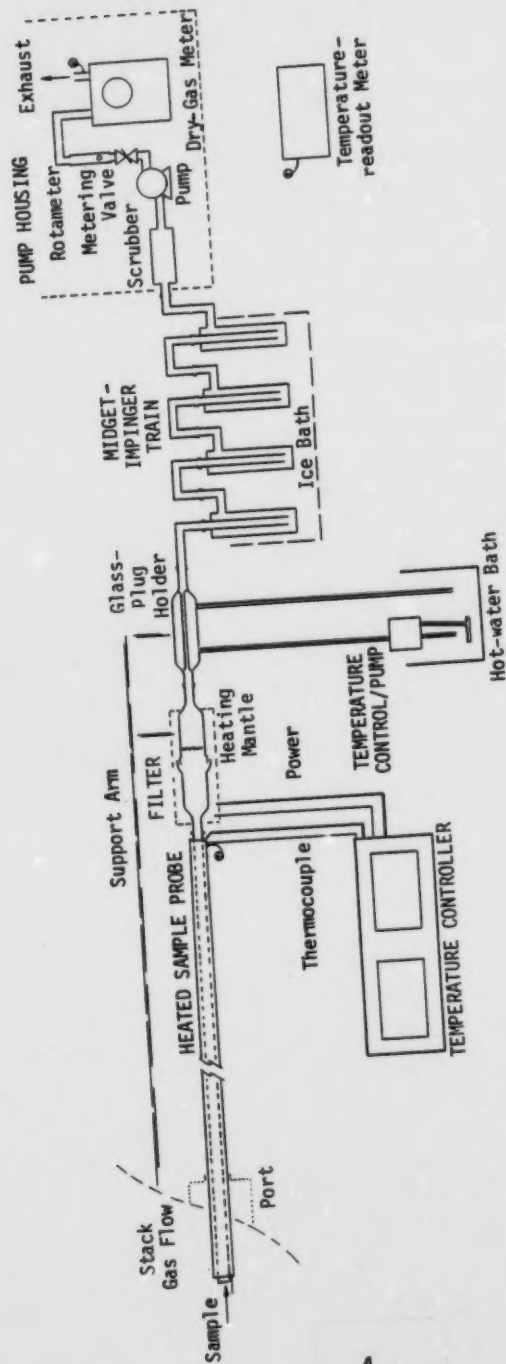


Figure 1. The Miniature Acid Condensation System.

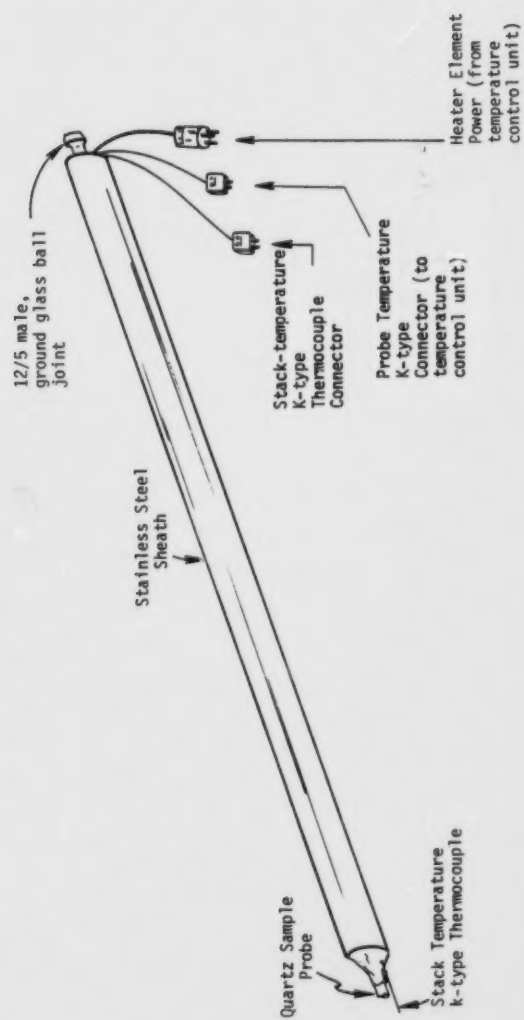


Figure 2. MACS heated quartz sample probe.

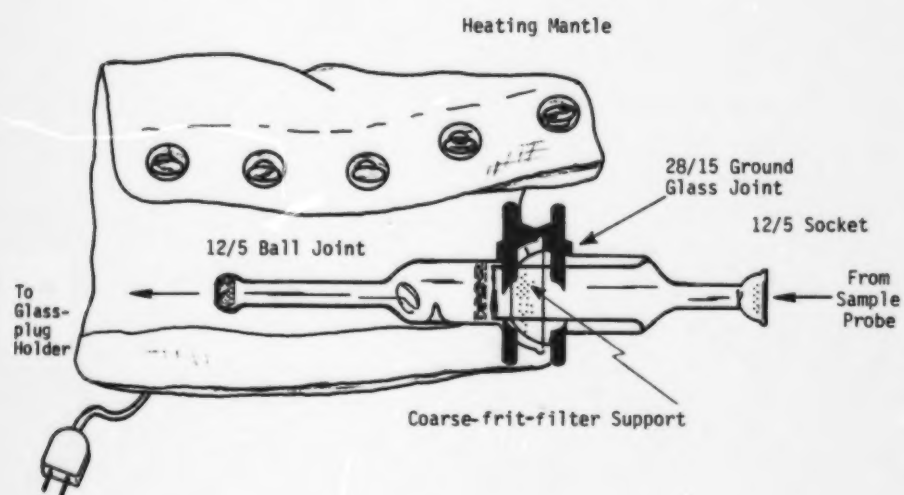


Figure 3. Quartz-filter holder.

Temperature-control Unit

The temperature-control unit (Figure 4) consists of two (2) electronic controllers which monitor the temperature and incrementally supply power to the sample-probe heating element and filter heating mantle, respectively.

Water-jacketed Glass-plug Holder

The water-jacketed glass-plug holder (Figure 5) is moderately packed with glass wool and insulated for sampling. The glass plug should be a minimum of 70 mm in length and be packed sufficiently tight to cause a nominal 112 mm Hg pressure drop at 3 l/min. flowrate. The insulation minimizes temperature loss and variation during sampling.

Constant-temperature Water Bath

The constant-temperature water bath (Figure 6) consists of a pump and heating unit, an insulated stainless-steel beaker, and interface tubing to the glass-plug holder.

Impinger Train/Ice Bath Component

The impinger train/ice bath component (Figure 7) includes an insulated container with removable lid which can accommodate up to four (4) midget impingers.

Sample Pump Unit

The sample pump unit (Figure 8) contains a flow controlling-type rotameter, replaceable silica-gel drying tube, lightweight pump, and a dry-gas meter. The dry-gas meter is equipped with an exit thermocouple.

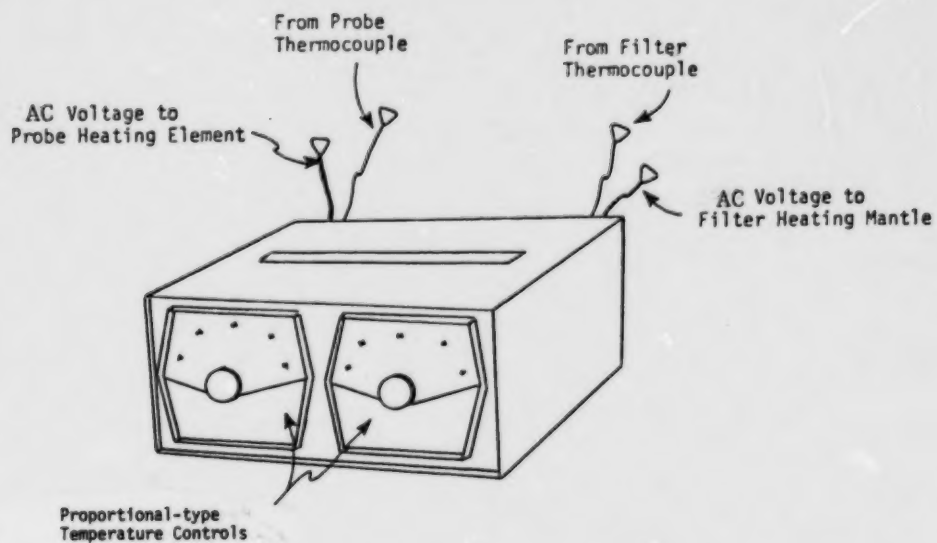


Figure 4. Probe/filter temperature-control unit.

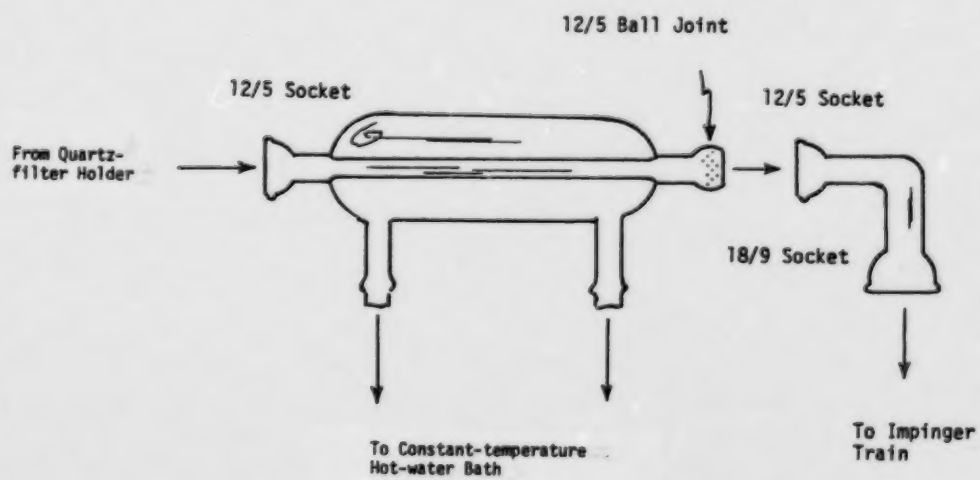


Figure 5. Glass-plug holder.

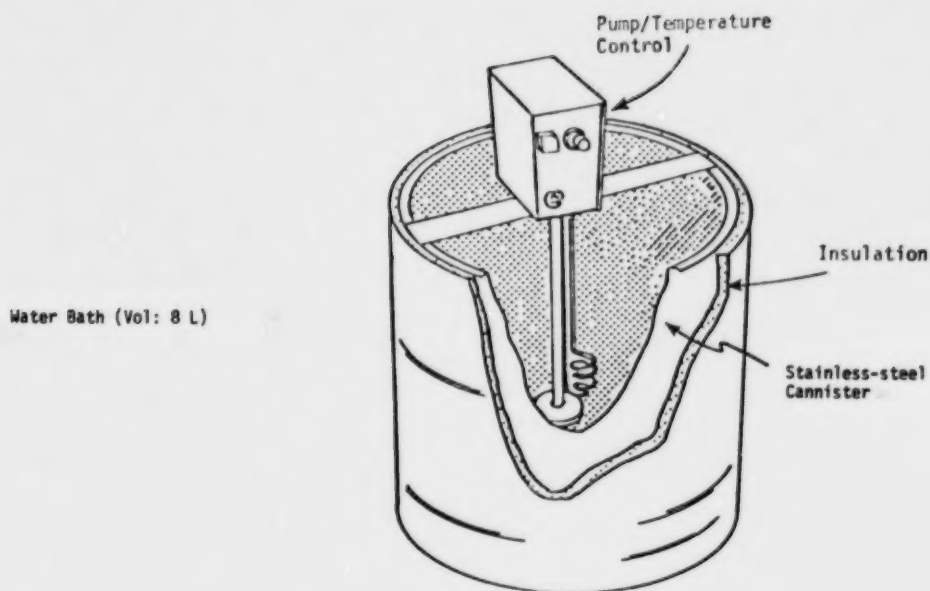


Figure 6. Constant-temperature water bath.

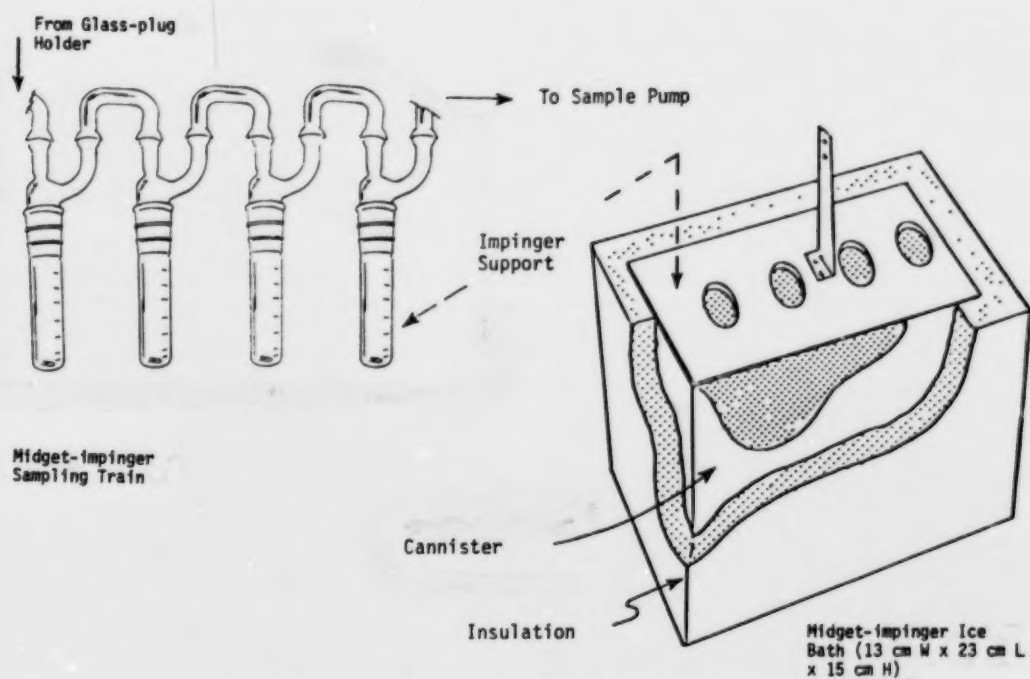


Figure 7. Impinger-train/ice bath.

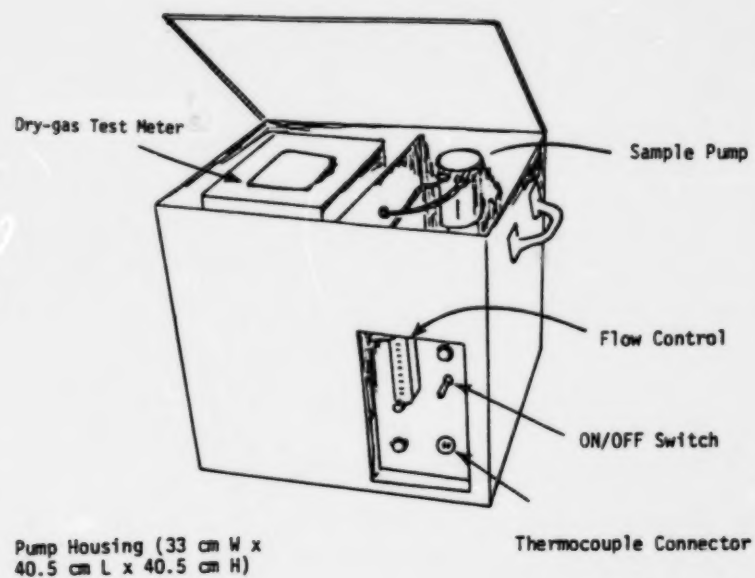


Figure 8. Sample pump unit.

SYSTEM FUNCTION

During operation of the MACS system, sample gas is extracted through the heated sample probe into the quartz-filter holder. The 16-mm quartz filter installed in the filter holder removes particles present in the gas sample. Both the filter holder and the probe are maintained at or above 271°C (520°F). The sample gas stream is cooled in the glass-plug holder to approximately 60°C (140°F). At this temperature, moisture and SO₂ present in the sample remain in the gas phase, and H₂SO₄ present in the sample collects in the glass wool plug.

The sample gas then passes through the midjet impingers containing H₂O₂ absorption solution where the SO₂ is oxidized and collected as sulfate ions (SO₄).

The balance gas is pulled through the drying tube and pumped through the rotameter and dry-gas meter. Normally a volume of from 28.3 to 56.6 l (1 to 2 ft³) of sample is collected; variation in the volume depends on the moisture content of the sample gas and on the method of sample analysis selected.

A filtered probe wash and a filter/filter holder front half wash with 100% isopropanol (IPA), along with the glass-plug catch, provide a gaseous H₂SO₄ measurement. The glass plug is always recovered using distilled H₂O.

Washing the probe and filter holder front-half and particle filter with water after the 100% IPA wash provides a water-soluble sulfate measure.

Analysis of the impinger catch for SO₄, either by barium thorin titration or by ion chromatography (IC), provides an SO₂ measurement. Thus, an SO₂ measurement and a gaseous H₂SO₄ measurement can be achieved. By recovering the particulate sulfates in the probe filter a total sulfate estimate can be made. If the fraction of the total SO₄ in the probe and filter which exist as H₂SO₄ is not to be recovered separately from metal sulfates, the probe and filter are recovered using 80% IPA/20% H₂O.

SECTION 3

SYSTEM OPERATION

EQUIPMENT ASSEMBLY

Actual sampling begins with the installation of the port cap and sampling-train support bracket. Insert the probe with the downstream end capped. Connect the appropriate thermocouple and power lines between the probe and temperature controller. Then turn on the temperature controller. The use of a cap on the rear of the probe, prior to assembling the remainder of the system, prevents any ambient air or stack gas from flowing through the probe which enhances rapid heating of the probe.

Install the quartz filter in the holder and give a slight twisting motion to the ball portion of the filter holder as it is inserted into the socket part of the holder. Hold two pieces (ball and socket) together with a locking (thumb-screw-type) pinch clamp. Then wrap the holder assembly in the heating jacket and suspend it from the support rack behind the probe. Connect the thermocouple and power lines to the second temperature controller and activate this controller. Install the pinch-clamp leak-check assembly onto the inlet end of the filter holder.

Following this step, prepare the glass-plug holder by connecting it to the water bath. Caution should be exercised in assuring that the glass-plug condenser completely fills with water being circulated from the water bath. To fill the condenser hold it "upside down" so that the bath-water inlet/outlet projects upward for a few seconds. Then suspend the condenser from the rack and, with a small amount of stopcock grease and a locking pinch clamp, attach it to the outlet end of the filter holder.

With the three temperature-controlled elements of the sampling train installed, the next step is to charge the ice bath and install the impinger train. Particulate SO_4 is collected in the probe and filter, H_2SO_4 is collected in the glass plug, and the SO_4 component SO_2 is collected in the impingers. Sulfur dioxide is collected with a 3% H_2O_2 solution. The charging of impingers depends on both the amount of SO_2 and SO_4 in the sample stream and the method selected to measure qualitatively the resulting SO_4 . With the recommended sampling rate of 3 l/min, a rapid buildup of H_2O in the first impinger may occur from condensation and can produce liquid carryover. A practical solution to this problem is to leave the first impinger dry, charge the second and third impingers each with 15 ml of 3% H_2O_2 , and leave the fourth impinger dry. Then ice down the impingers and mount the system on the rack behind the filter holder and condenser. Attach the impinger train to the glass-plug holder (upstream) and to the sample pump (downstream) and proceed with a system leak check.

SAMPLING PROCEDURE

To begin the leak check pinch a flexible tube attached to the inlet of the filter holder and start the pump. With a vacuum of 250 mm Hg (10 in Hg) the leak rate should be less than 2% of the average sampling rate. Unlike the U. S. Environmental Protection Agency Standard Reference Method 6 procedure, however, leak checks must be performed both prior and subsequent to sampling. Both checks are necessary because a leak may occur in the filter-holder 28/15 ball and socket which is used without stopcock grease. Releasing the vacuum across the impinger system following the leak check should be done cautiously and gradually by releasing the pinch clamp in front of the filter holder. With the vacuum released, the pump can be stopped without any backflushing in the impingers.

After recording the gas-meter start volume, start time, and system temperatures, connect the filter to the probe exit and initiate sampling. Depending on the method of analysis, from 1 ft^3 to 4 ft^3 of sample at a rate of 3 l/min can be collected (1 ft^3 = 28.3 liters). The actual volume of sample collected is discussed under the section on sample analysis.

SAMPLE RECOVERY AND ANALYSIS

At the end of the sampling run, the following procedure is recommended for best sample recovery. After recording the temperatures, time, and gas-meter volume, deactivate the two temperature controllers and turn off the water bath circulator. Separate the probe from the filter holder and then install the probe cap and leak-check ball on the probe exit and filter-holder inlet, respectively. With the pinch clamp closed and the correct gas-meter volume recorded, start the pump box for the concluding leak check. While the vacuum is forming, disconnect the thermocouple and power lines from the temperature controllers as well as the water lines to the condenser. Finally, after completing the leak check, remove the filter-holder assembly, condenser, and impingers to the sample-recovery area.

To conserve time, a duplicate set of components are recommended to allow subsequent sampling to be run while the first sample train is being recovered. If the probe is to be recovered (see option discussed in section on data interpretation), remove it just after removing the filter, condenser, and impingers to allow cooling to take place. In the recovery area, open the filter-holder heater to allow the holder and clamp to cool more rapidly.

Recovery of the Glass Plug

Mount the glass-plug holder and recovery flask on a ringstand and pull 10 ml of solvent (distilled H_2O) into the plug. It is recommended that this initial 10 ml be left in the plug while the impinger system is being recovered. Following the recovery, pull the initial 10 ml into the flask and pull two additional 10 ml aliquots through the plug. Then transfer the total 30 ml to the shipping and/or analysis container. After this transfer, rinse the plug with two 10 ml aliquots of 100% isopropanol. After rinsing, pull air through the plug using the vacuum. The 100% IPA rinse is strictly for the purpose of drying the plug, and the rinse should be discarded.

Recovery of the Impingers Catch

Whether or not the first impinger contains H_2O_2 , it is recommended that the following impinger recovery procedure be followed. Rinse all four impingers as well as U-tubes and combine all solutions. Also rinse the glassware connecting the condenser to the first impinger into the impinger catch. Following collection of all impinger recovery solutions and rinses into the shipping and/or analysis container, recharge the impinger system for any subsequent run.

Filter and Filter-holder Wash

After cooling the filter, remove it from the holder and place it in the shipping and/or analysis container. Rinse the filter-holder surfaces into this same container, using 80% IPA/20% H_2O . Then cap the container and shake to assure wetting of the entire filter and particles. Rinse the filter holder with 100% isopropanol to remove any moisture on the surface of the holder, then install a new filter and reassemble the holder. The filter rinse should be filtered through a SO_4 -free filter into the proper volumetric flask prior to dilution and analysis.

Probe Wash

Following an adequate cooling period, recover the probe by washing into the shipping and/or analysis container, using 80% IPA/20% H_2O . As with the filter solution, filter the probe-wash solution prior to volumetric dilution and analysis. After washing the probe with water, rinse it with 100% isopropanol.

Alternate Filter- and Probe-wash Method

A procedure to recover the sampling-train fractions can be followed to separate absorbed H_2SO_4 from metallic sulfates. The procedure involves washing the filter, filter holder, and probe through a SO_4 -free filter media using 100% IPA. This recovers the H_2SO_4 alone. Following this, the

particles can be washed with 80% IPA/20% H₂O to recover the remaining water soluble sulfates separately.

SAMPLE ANALYSIS

Analysis of the recovered fractions is nearly always conducted by barium thorin titration, as described in EPA Standard Reference Method 6, or by IC. It is recommended that the highly sensitive method of IC be used, (especially for the probe, filter, and plug washes) for sources with low primary-sulfate emissions. In addition, titration of the probe and filter with barium thorin may require passing the sample through a cation-exchange resin to remove metals that interfere with the endpoint. Procedures for barium thorin titration and IC are presented in Appendices A and B, respectively.

To minimize the number of sample analyses, the probe wash and filter catches can be combined to provide a total particulate SO₄.

DATA HANDLING PROCEDURE

Calculation of SO₂, H₂SO₄, and metallic sulfates provides concentrations in terms of mass/standard reference volume. The mass concentration of SO₂ is based on the molecular weight of 64.06 g/mol. The mass concentration of H₂SO₄ is based on the molecular weight of 98.08 g/mol. If the alternative sample recovery method is chosen, a total H₂SO₄ can be calculated by adding the 100% IPA-recovered acid from the probe and filter particles to that collected in the glass plug. The remaining sulfates recovered as water soluble are calculated using the mass of 98.08 g/mol. This is a minimum weight concentration since all of the metal sulfates such as Na, K, Ca, Mg, Fe, and V are heavier. This simplified calculation is made since sophisticated analyses are necessary to distinguish these metal sulfate salts.

The results of sulfur-oxide measurements which distinguish H_2SO_4 - SO_4 salts, or simply total SO_4 , are often used to compare the relative amount of original SO_2 to that converted to SO_4 . This ratio is often expressed as percent conversion of SO_2 to SO_4 and is generally expressed as:

$$\frac{\text{SO}_4 \text{ concentration}}{\text{SO}_2 + \text{sulfate concentration}} \times 100.$$

These conversion calculations can be misleading, however, because they depend on what concentration units are used in the formula.

Two examples of conversion calculations appear below, using mg/dscm concentrations:

$$\text{A. \% conv.} = \frac{19 \text{ mg H}_2\text{SO}_4/\text{dscm}}{380 \text{ mg SO}_2/\text{dscm} + 19 \text{ mg H}_2\text{SO}_4/\text{dscm}} \times 100\% = 4.77\%$$

$$\text{B. \% conv.} = \frac{(0.327) 19 \text{ mg H}_2\text{SO}_4/\text{dscm}}{(0.50)380 \text{ mg SO}_2/\text{dscm} + (0.327)19 \text{ mg H}_2\text{SO}_4/\text{dscm}} \times 100\% = 3.17\%$$

Calculation A determines percent conversion using only the mass/volume concentrations, which include the additional oxygen weight in the H_2SO_4 that accounts for the larger percentage.

Calculation B converts the mass concentrations to the concentration of sulfur only, $(\frac{\text{wt. of sulfur}}{\text{wt. of component}})$ (component concentration), and the results reflect the fraction of sulfur atoms which are converted to the higher oxides.

The calculation method used is not important unless separate results are to be compared. Then the data analyst must take into account the derivation of conversion rates.

SECTION 4

MACS SYSTEM FABRICATION

This section presents parts and materials specifications and assembly instructions for each component part of the MACS system. Many of the parts and materials discussed in this section and listed in Section 5 (Parts List) are identified by specific part number and possible vendor. Substitution or modification of parts or materials depends on many factors such as accessibility and cost, and therefore can be done at the discretion of the user.

SAMPLE PROBE

Figure 9 illustrates the MACS heated quartz sample probe. The probe consists of a quartz tube wrapped with a heating tape, a probe-temperature thermocouple, and a stainless-steel sheath.

Parts and Materials Specifications

Probe:	Quartz tube, 6 mm O.D. x 81 cm length, with 12/5 female ground glass ball joint and thermocouple well 31 cm from upstream end.
Heating Tape:	Standard heating tape, 1.3 cm x 18.3 cm, 288 w, 482°C maximum, two-piece connector.
Sheath:	Thin wall, 304 stainless steel; 25.4 mm O.D.
Thermocouple(s):	Two (2) k-type thermocouples (1 x 100 cm, 1 x 70 cm) fitted with miniature male T.C. connectors.
Fabrication Materials:	High-temperature glass tape. Epoxy adhesive/sealant.

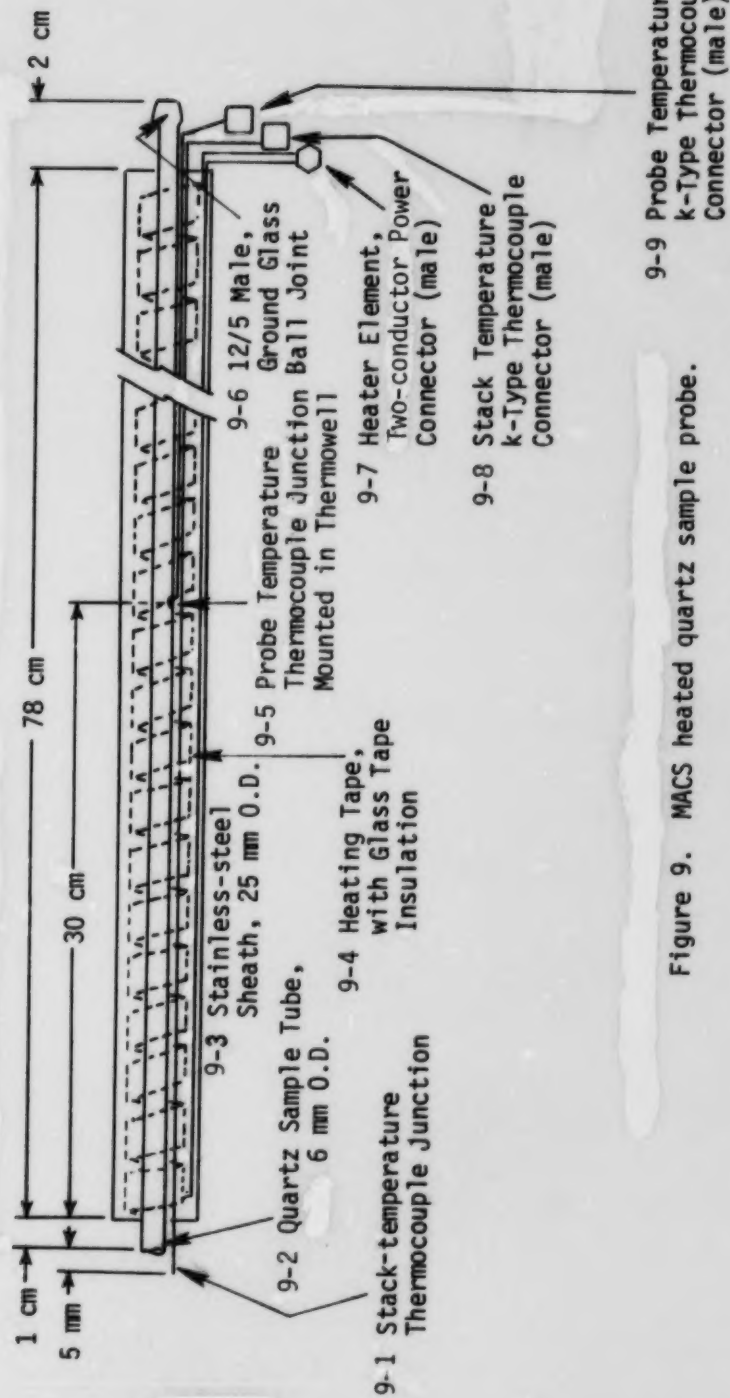


Figure 9. MACS heated quartz sample probe.

Assembly

- Secure the stack-gas-temperature thermocouple to the quartz sample tube with high temperature glass tape, allowing the end of the thermocouple to extend approximately 5 mm past the upstream end of the sample tube.
- Position the probe temperature thermocouple in the temperature well located on the quartz sample tube and secure it in a similar manner as above.
- Secure the heating tape to the sample tube with glass tape, starting approximately 1 cm from the inlet end of the sample tube. The entire heating tape should be wrapped with the high-temperature glass tape, providing insulation between the heat tape and the stainless-steel sheath. Cut the heating tape leads and splice them (prior to wrapping the sample tube) to lengths of 20 cm and 100 cm, respectively. Each splice should be insulated with the glass tape and secured firmly to the sample tube with additional glass tape.
- Insert the probe assembly in the stainless-steel sheath and secure the ends with epoxy adhesive. The sample tube should extend 1 cm past the sheath at the inlet end and approximately 2 cm past the sheath at the outlet end.

QUARTZ-FILTER HOLDER

Figures 10 and 11 give a scale drawing of the quartz-filter holder. The quartz-filter holder is fabricated with a 28/15 quartz joint, modified with a coarse-frit quartz-filter support. The unit is heated with a jacket-type heating mantle, illustrated in Figure 12.

Parts and Materials Specifications

- | | |
|-----------------|---|
| Filter Holder: | Ball-and-socket 28/15 ground glass joint. Ball-and-socket 12/5 ground glass joint. Coarse frit-filter (quartz parts used throughout). |
| Thermocouple: | One (1) k-type thermocouple (10 cm L with miniature male T.C. connectors). |
| Heating Jacket: | Tubular Jacket type, 150 mm L x 150 mm W x 50 mm thick, 115 VAC, 175 W with a two-prong (M) AC connector. |

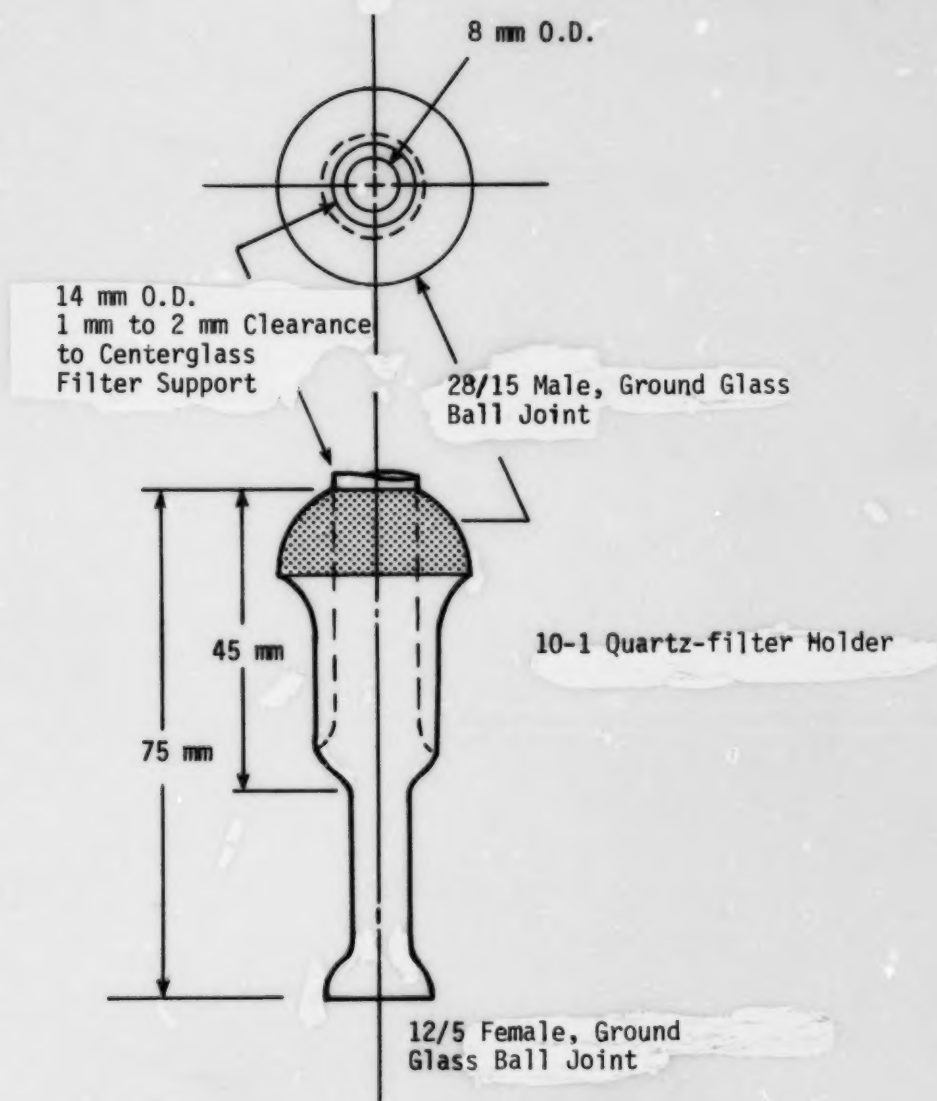


Figure 10. Quartz-filter holder (upstream half).

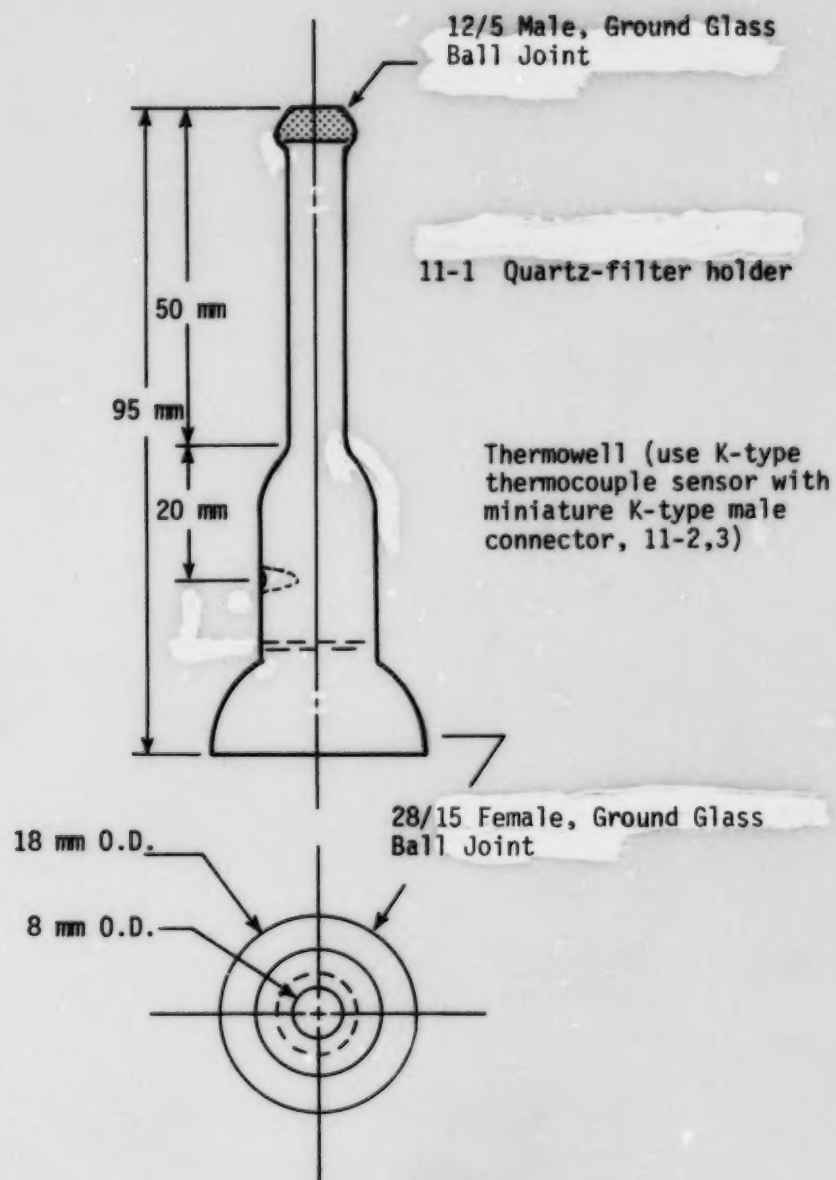


Figure 11. Quartz-filter holder (downstream half).

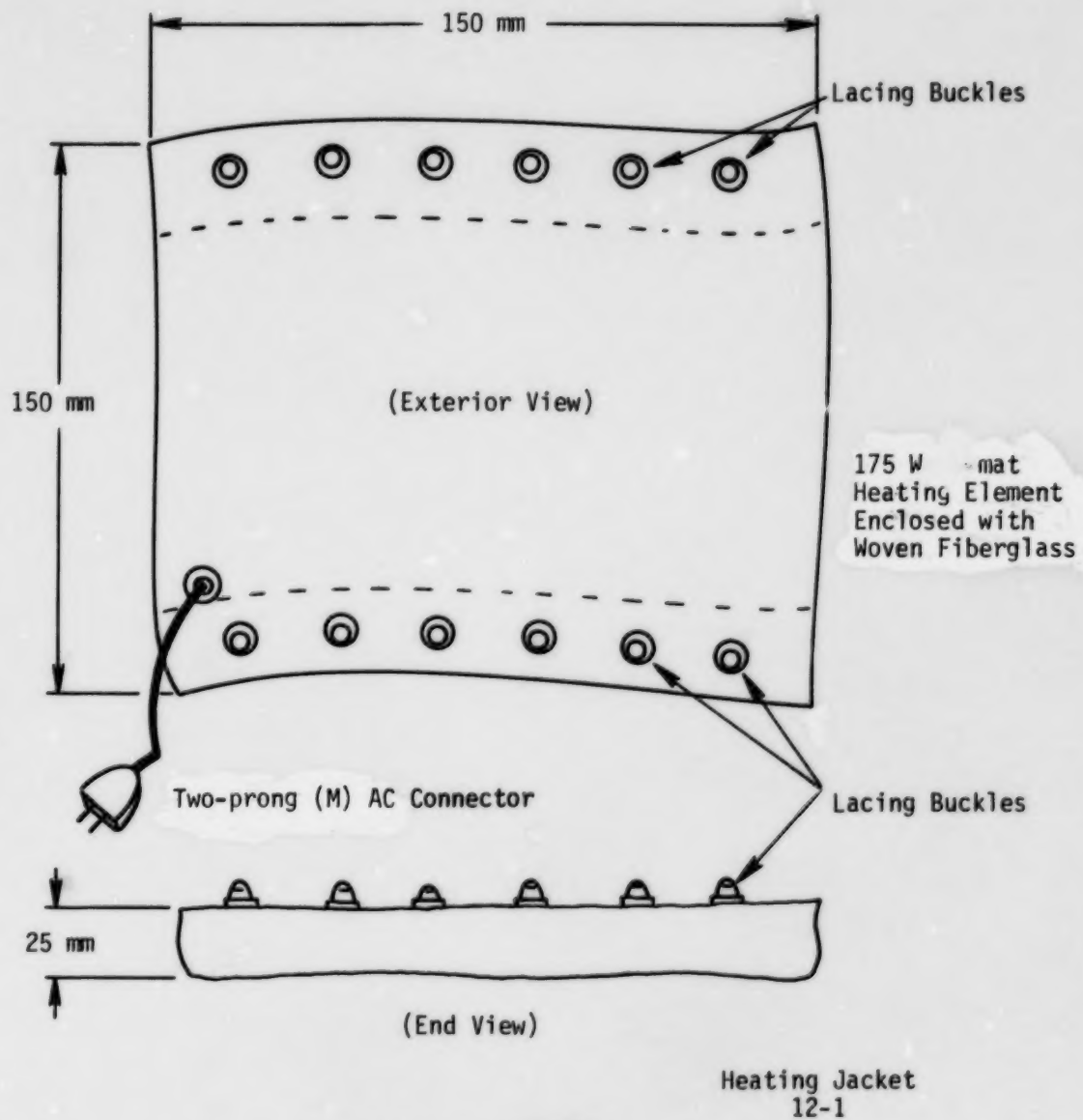


Figure 12. Filter-holder tubular heating jacket.

Assembly

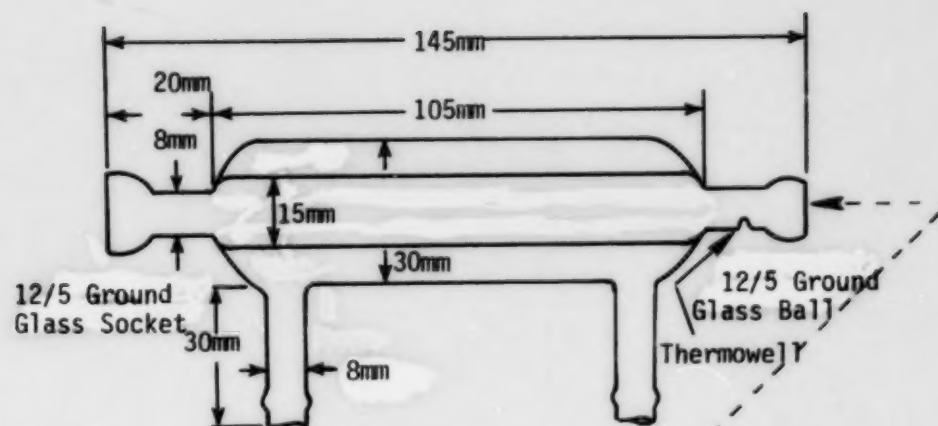
- Fit the 28/15 ground glass ball joint with a 12/5 socket and a glass-tube filter support as shown in Figure 10. Cut the tube filter support to allow 1 mm to 2 mm clearance from the coarse frit mounted in the downstream half of the assembly. (The tube filter support holds the filter in place during no flow periods.)
- Fit the 28/15 socket with a coarse-frit-filter support and a 12/5 ball joint as shown in Figure 11. An indentation in the glass wall downstream from the frit provides a thermowell for the thermocouple.
- The jacket-type heating mantle shown in Figure 12 consists of a 175-W mat-heating element enclosed with woven fiberglass. Lacing buckles are positioned on two edges, and power is applied via a two-prong (M) AC connector.
- Section 3 (System Operation) discusses the installation of the 16 mm high purity quartz filter used in the holder during sampling.

GLASS-PLUG HOLDER

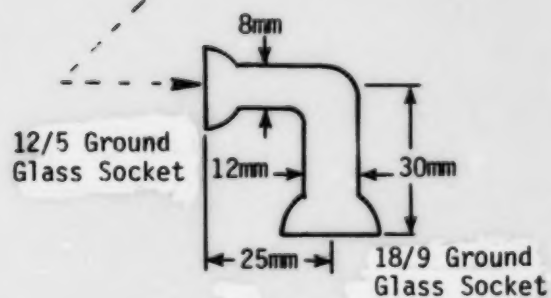
Figure 13 is an illustration of the glass-plug holder. The unit is fitted with outlet and inlet 12/5 ball-and-socket ground glass joints, respectively, and with tube fittings to the constant-temperature hot-water supply. Figure 13 also shows a glass elbow used to connect the glass-plug holder to the midjet-impinger train.

Parts and Materials Specifications

- | | |
|--------------------|---|
| Glass-plug Holder: | 4 mm, 8 mm, and 30 mm Pyrex® tubing, Pyrex® 12/5 ball, and 12/5 socket ground glass joints. |
| Reducing Elbow: | Pyrex® reducing elbow, 12/5 to 18/9 ground glass sockets. |
| Insulation: | Any type of thermal insulating material, e.g., aluminum-foil duct tape. |



Construction: Pyrex
 Insulation: 13.3 Thermal Insulating Tape



13.2 Reducing Connector
 (Plug-holder-to-impinger)

Figure 13. Glass-plug holder.

Assembly

- Fabricate the glass-plug holder to the size and dimensions given in Figure 13.
- Wrap the entire unit with a thermal insulating material, such as aluminum foil duct tape.
- Section 3 discusses the addition of the glass plug to the holder.

MIDGET-IMPINGER TRAIN

The midget-impinger gas-sampling train consists of four (4) 30 ml midget impingers connected in series with glass u-tube connectors. The final impinger is connected to a gas pump with a stainless-steel quick-connect-type fitting. Figure 14 shows a typical midget impinger, u-tube connector, and the final quick-connect fitting. During sampling, the train is partially submersed in an insulated ice bath (in Figure 15).

Parts and Materials Specifications

- Midget Impingers: Four (4) 30-ml Pyrex® midget impingers with inlet/outlet 18/9 ground glass ball joints.
- Connectors: Three (3) Pyrex® u-tube connectors with inlet/outlet 18/9 ground glass sockets. One (1) 18/9 Pyrex® ground glass socket-to-stainless-steel quick-connect fitting.
- Ice Bath: Aluminum can, 16-gage, welded seams (100 mm W x 200 mm L 150 mm H, with 25 mm Lip). Aluminum support bracket, 10-gage (50 mm W x 250 mm L, with four (4) equally spaced 25 mm holes. Support arm, 16-gage aluminum (25 mm W x 156 mm L), Insulating Foam (1 m² x 25 mm thick), Duct tape.

Assembly

- Bolt or rivet the impinger support to the lip of the "ice bath" aluminum can. Attach the support arm to the center of the impinger support in a similar manner.
- Cover the outside of the can with approximately 25-mm thick polystyrene or polyurethane insulating foam. The foam can be held adequately in place with furnace duct tape.

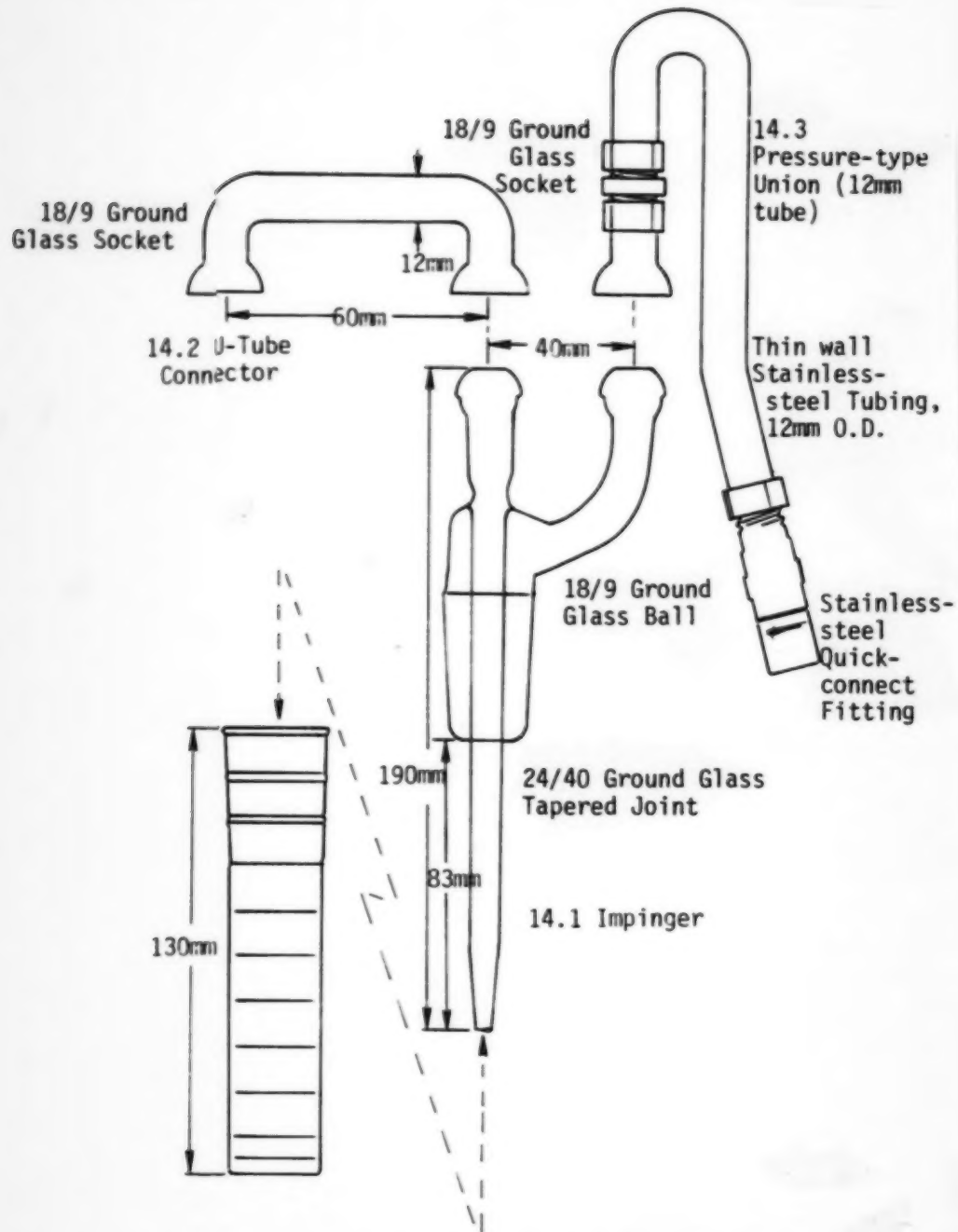


Figure 14. Impinger, u-tube connector, and quick-connect fitting.

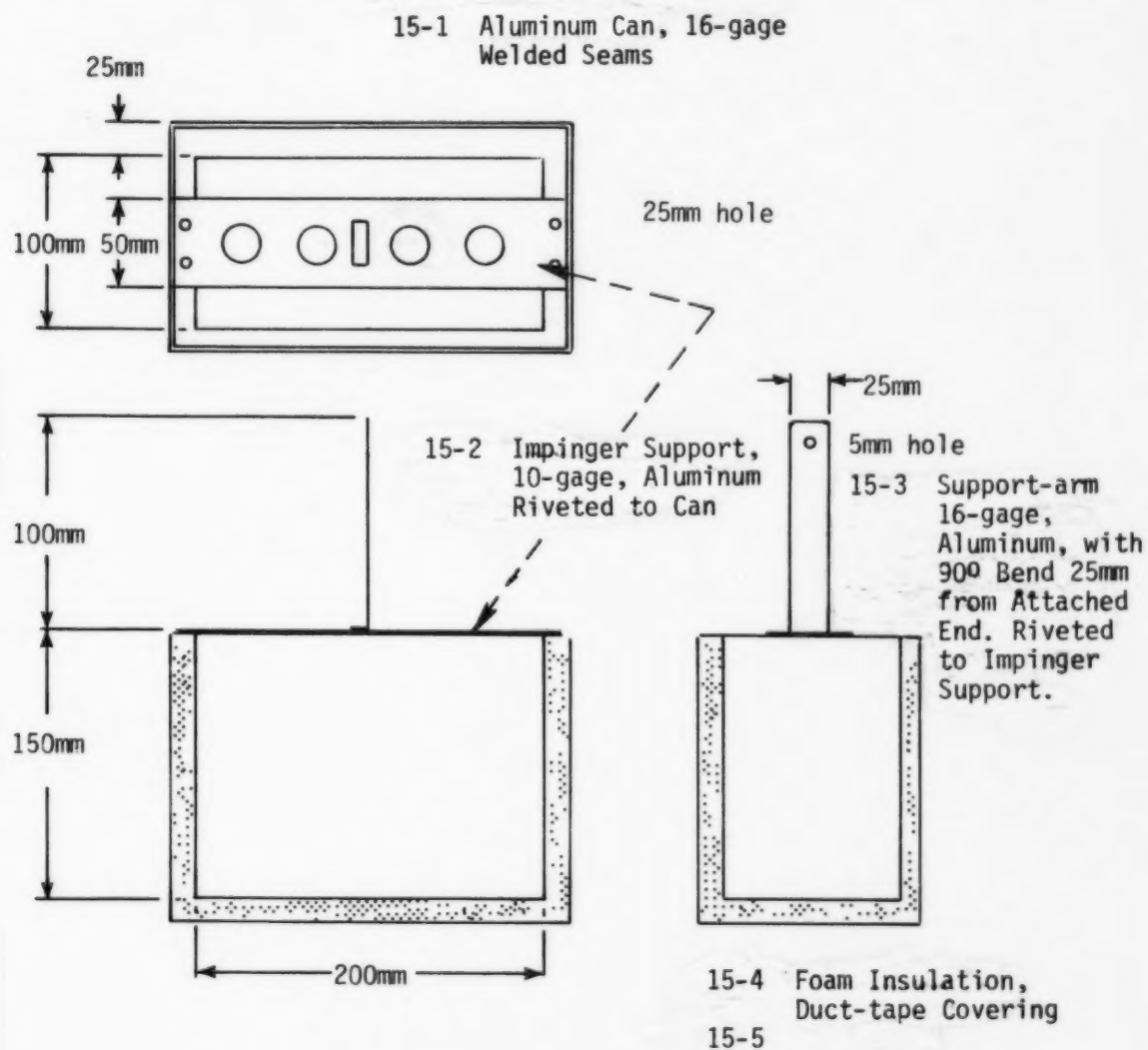


Figure 15. Insulated ice bath.

SAMPLE PUMP/METERING UNIT

Figure 16 demonstrates a functional drawing of the sample pump/metering unit. The gas sample is pumped from the impinger train through the quick-connect connector and umbilical tube, through a scrubber to the sample pump. The sample-gas flow rate is adjusted via a metering valve/variable flow rotameter and recorded with a dry-gas test meter. A k-type thermocouple is mounted in the gas stream at the outlet connector of the dry test meter. The interface connectors to the unit (e.g., power, temperature, gas lines) and the flow-control valve are panel mounted on an outside wall of the pump housing. The entire system is mounted in an aluminum carrying case, shown in Figure 17. Figure 18 shows the gas sample umbilical tube used to connect the impinger train to the pump unit.

Parts and Materials Specifications

Housing:	0.090 in. aluminum, welded seams (Figure 17).
Sample Pump:	Vacuum/pressure type; vacuum to 20" Hg., pressure to 18 psi, free-air capacity greater than 1000 in. ³ /min, 3/8 in. (F) NPT ports.
Meter Valve/Rotameter:	0.5 l/min to 5 l/min., panel mount; 1/8 in. (F) NPT ports.
Dry-gas Test Meter:	Capacity - 200 SCFH
Temperature Sensor:	K-type thermocouple with panel mount miniature (M) thermocouple connector.
Drying Tube:	Polyethylene drying tube (200 mm L x 16 mm I.D.) with end pieces modified for pressure-type tube connection (1/4 in. tube)
Plumbing:	Stainless-steel pressure-type fittings and 6.35 mm O.D. stainless-steel interconnecting tubing.
Electrical:	Panel mount fuse holder, 1.5 amp fuse, panel mount SPST AC switch (6 amp. 125 VAC, 3 amp. 250 VAC). Three-prong panel mount AC connector (M), power cord.

Fabrication Parts
and Materials:

Piano-type hinge (40 cm L), Two (2) door-pull handles, one (1) draw-catch latch, miscellaneous hardware. Rigid polystyrene foam.

Assembly

- Fabricate the pump housing from schedule-90 aluminum (welded seams) according to the dimensions shown in Figure 17. A recessed panel is provided for mounting controls and connectors and an interior panel is used to secure the dry-gas meter. Fix the housing cover to the housing with a piano type hinge and a draw-catch latch. Then attach door-pull handles to two sides and make a cutout section in one side, allowing access to the dry-gas meter readout panel. Actual placement of the cutout depends on the type of dry-gas meter used.
- Shock-mount the dry-gas meter and hold in place with rigid foam wedged between the meter and the sides and bottom of the housing. (Figure 19)
- Bolt the sample pump directly to the housing wall with the diaphragm end of the pump oriented toward the top to facilitate maintenance at a later time (Figure 19).
- Install the rotameter, quick-disconnect gas inlet, thermocouple connector, power switch, and fuse on the recessed control panel and panel mount the power connector on the rear side of the housing. Position the thermocouple junction in the dry-gas meter exhaust stream.
- Connect the panel-mounted power connector to the fuse, on/off switch, and pump using number 16-gage, stranded wire with a minimum of 150 V insulation voltage rating (Figure 16). Use a 2-amp, 250 V AGX type or equivalent fast-acting fuse to protect the wiring circuit.
- Plumb the system as shown in Figure 16. Stainless-steel tubing and fittings should be used throughout with the exception of the polyethylene drying tube. During periods of sampling, charge the drying tube with an indicating silica gel.

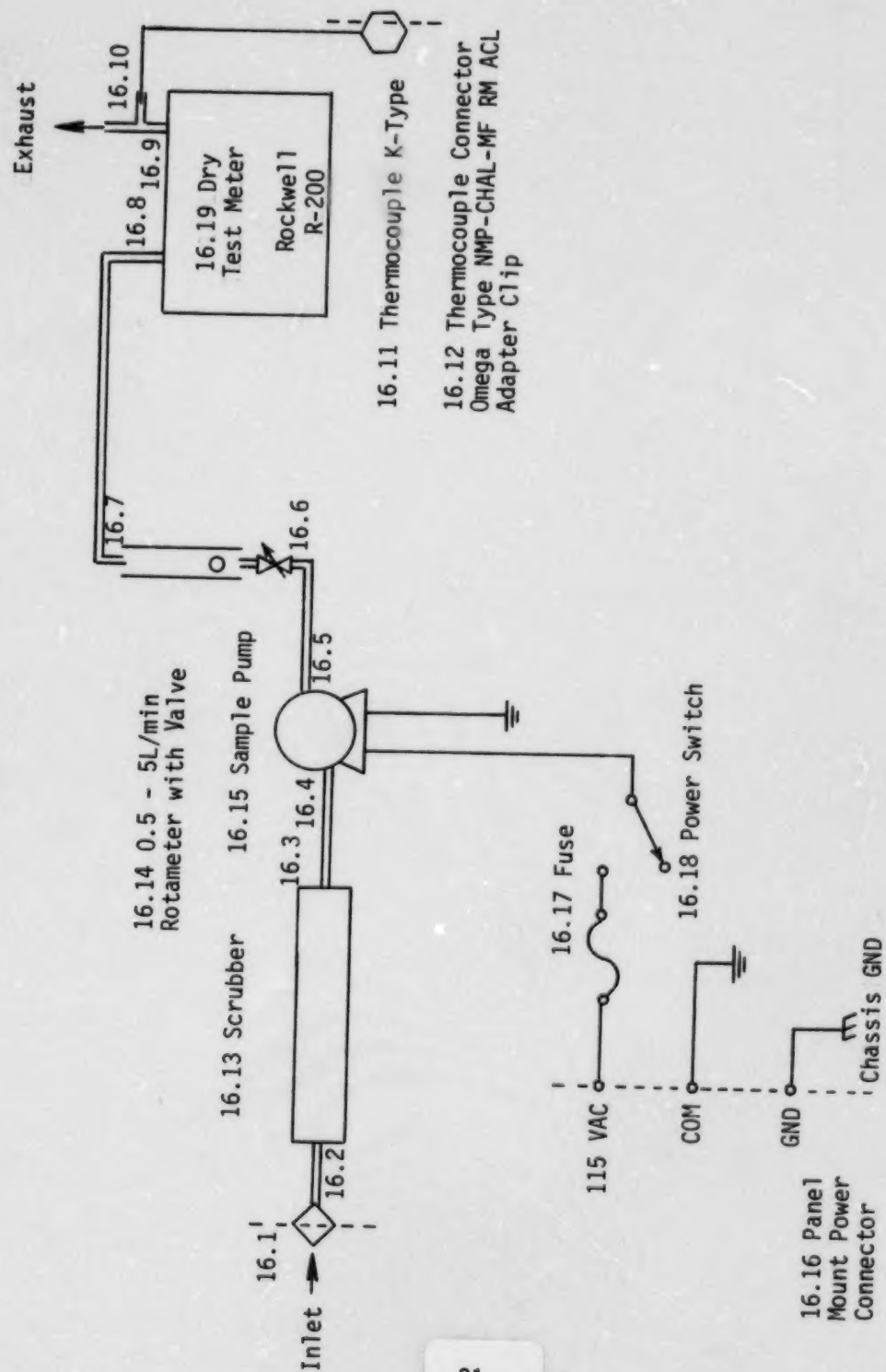
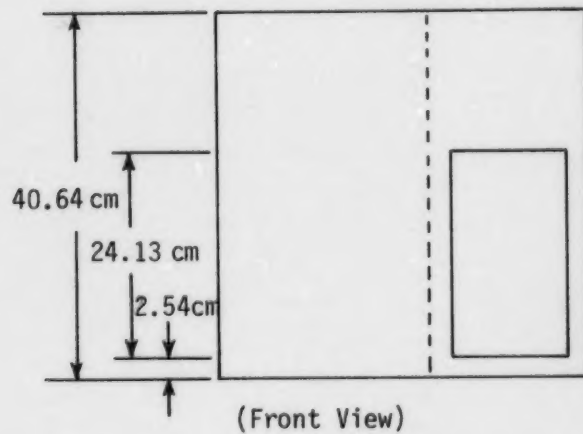
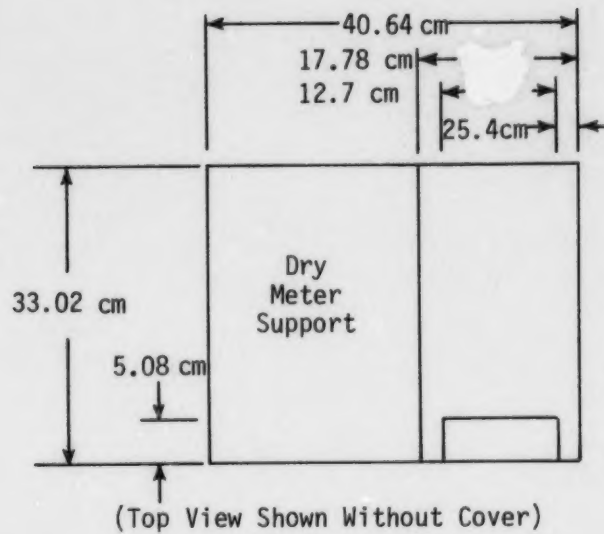
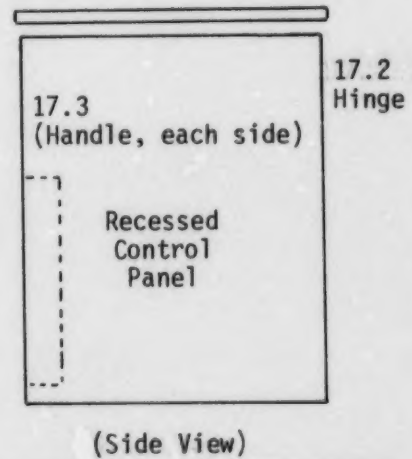


Figure 16. Sample pump unit.



Latch



Cover: Overlaps
Top with 8mm
Flange

17.1
DRY TEST METER PUMP HOUSING
Construction: 0.090 in.
Welded Aluminum

Figure 17. Sample-pump-unit housing.

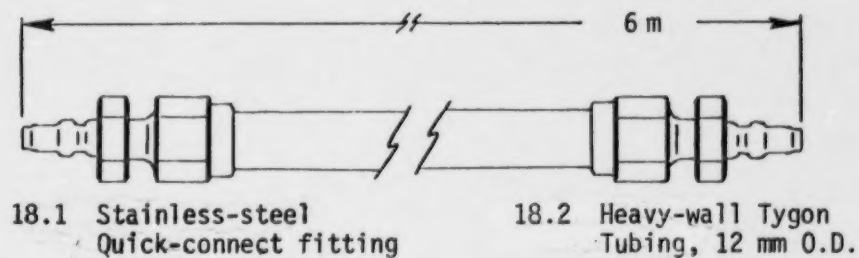


Figure 18. Umbilical tubing (pump unit-to-impinger train).

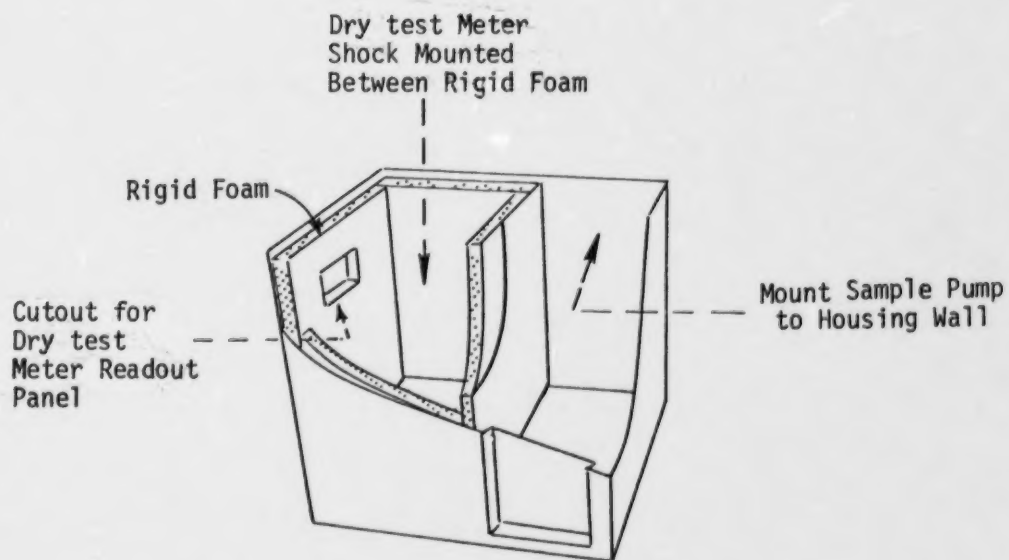


Figure 19. Dry-gas meter and sample pump installation.

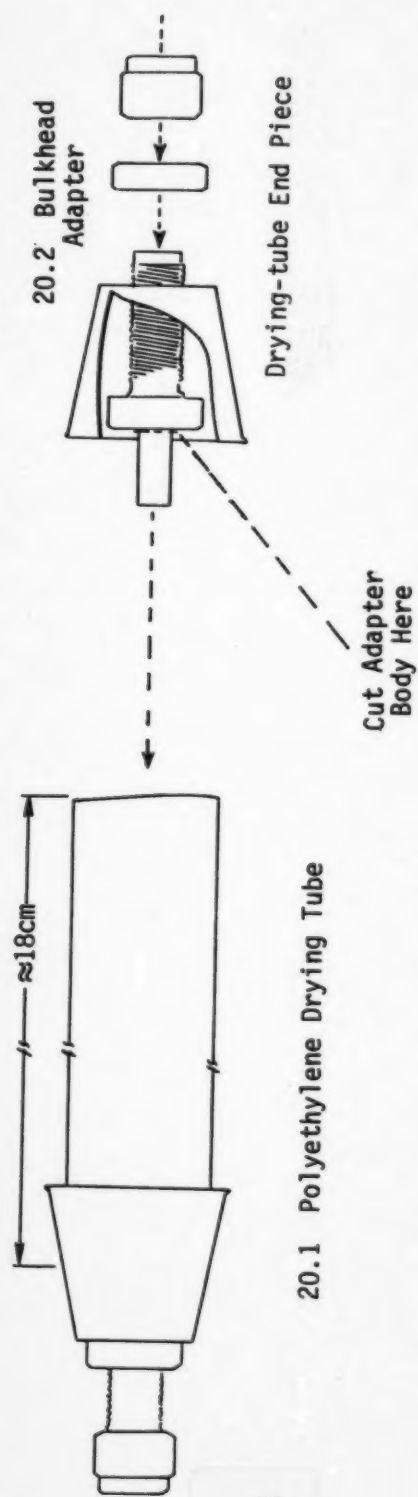


Figure 20. Drying-tube assembly.

TEMPERATURE CONTROLS

Four areas of the sampling system are temperature controlled, the probe, quartz-filter holder, glass-plug holder, and impinger train. The impinger train is kept chilled with an ice bath as discussed earlier in this section. The sample probe and quartz-filter holder are heated with electrical-resistive-type heaters which are controlled electronically with proportional heater controls. The glass-plug holder is controlled thermally with a circulating hot water bath.

The assembly of the proportional heater controls and the hot water bath are discussed in this section. Two proportional controllers are used to control the probe temperature and the filter-holder temperature respectively. Both units are mounted in a single carrying case, shown in Figure 21. Figure 22 shows the circulating hot water bath assembly.

Parts and Materials Specifications (Probe/Filter Controllers)

- | | |
|---------------------------|--|
| Proportional Controllers: | Two (2) proportional-type temperature controllers, K-type thermocouple calibration, 0°F - 600°F. range. |
| Housing: | Shadow cabinet (39 cm W x 23 cm D x 15 cm H), nominal dimensions: 16-gage panel with 18-gage cover, steel or aluminum. |
| Electrical: | K-type thermocouple wire with miniature (F) inline connector (2 x 2m), 14-3 power cord, 14-2 power cord with two-prong (F) inline connector (2m x 2m). |

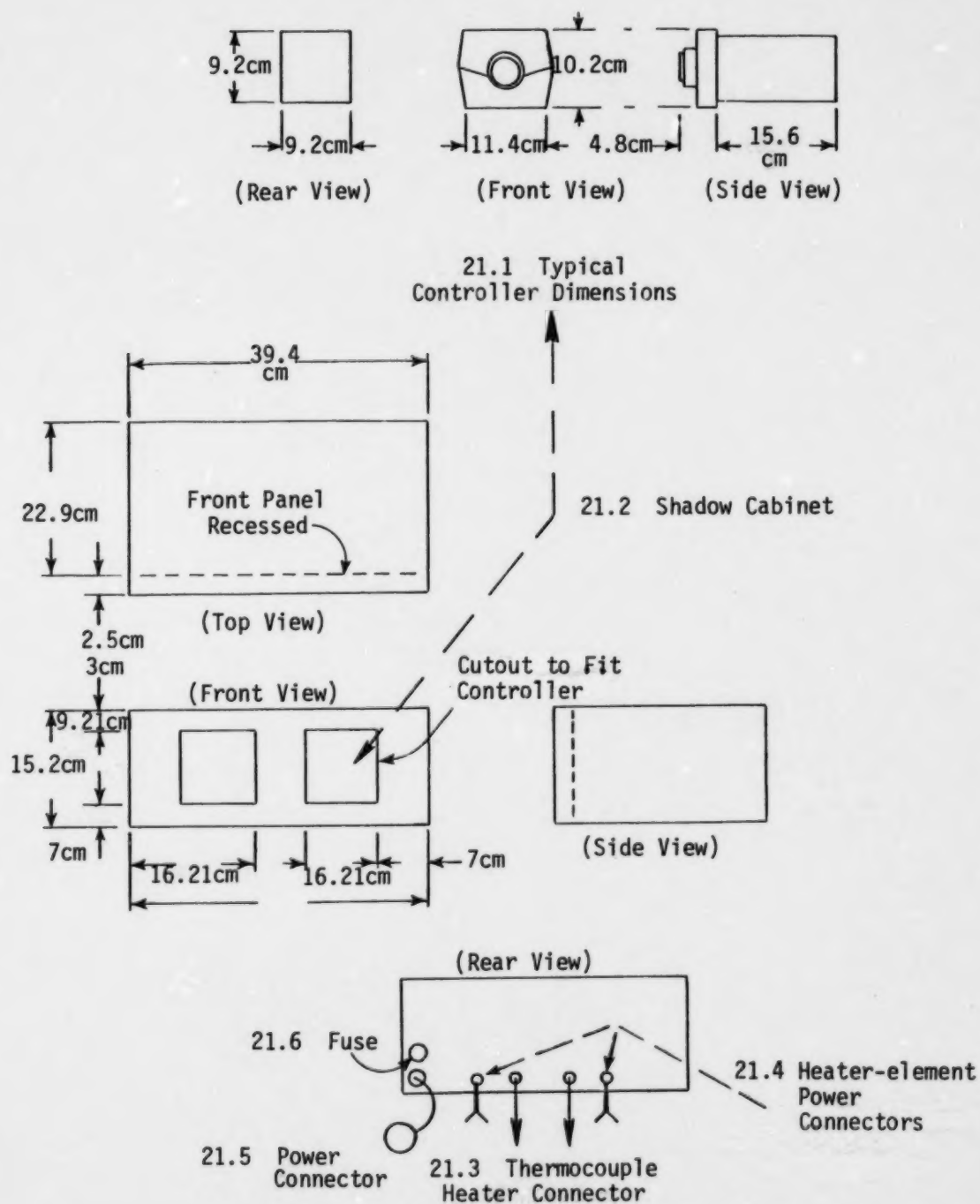


Figure 21. Proportional heater-control cabinet.

Parts and Materials Specifications (Circulating Bath)

Temperature Control/Pump:	Constant-temperature immersion circulator type, 30°C to 100°C. Range, $\pm 0.03^\circ\text{C}$. accuracy.
Water Bath:	Stainless-steel can, with 2.5 cm foam insulation, 8 liter minimum capacity.
Tubing:	1.25 cm O.D. heavy wall Tygon tubing (2 m-length) with stainless-steel hose-clamp fastners.

Assembly (Probe/Filter Controllers)

The two (2) proportional temperature controllers are mounted in a recessed front panel cabinet as shown in Figure 21. The recessed front panel provides a measure of protection against controller damage during shipping. The interconnecting thermocouple and power lines to the probe and filter holder should be strain relieved through the housing's rear panel.

Assembly (Circulating Bath)

The container used for the water bath should be insulated with a semi-rigid foam which can be secured in place with heat-duct tape. The controller is positioned in the bath with a support plate (Figure 22) which can be either fixed to the controller or fixed to the can. The latter will require a means of securing the controller in place during use.

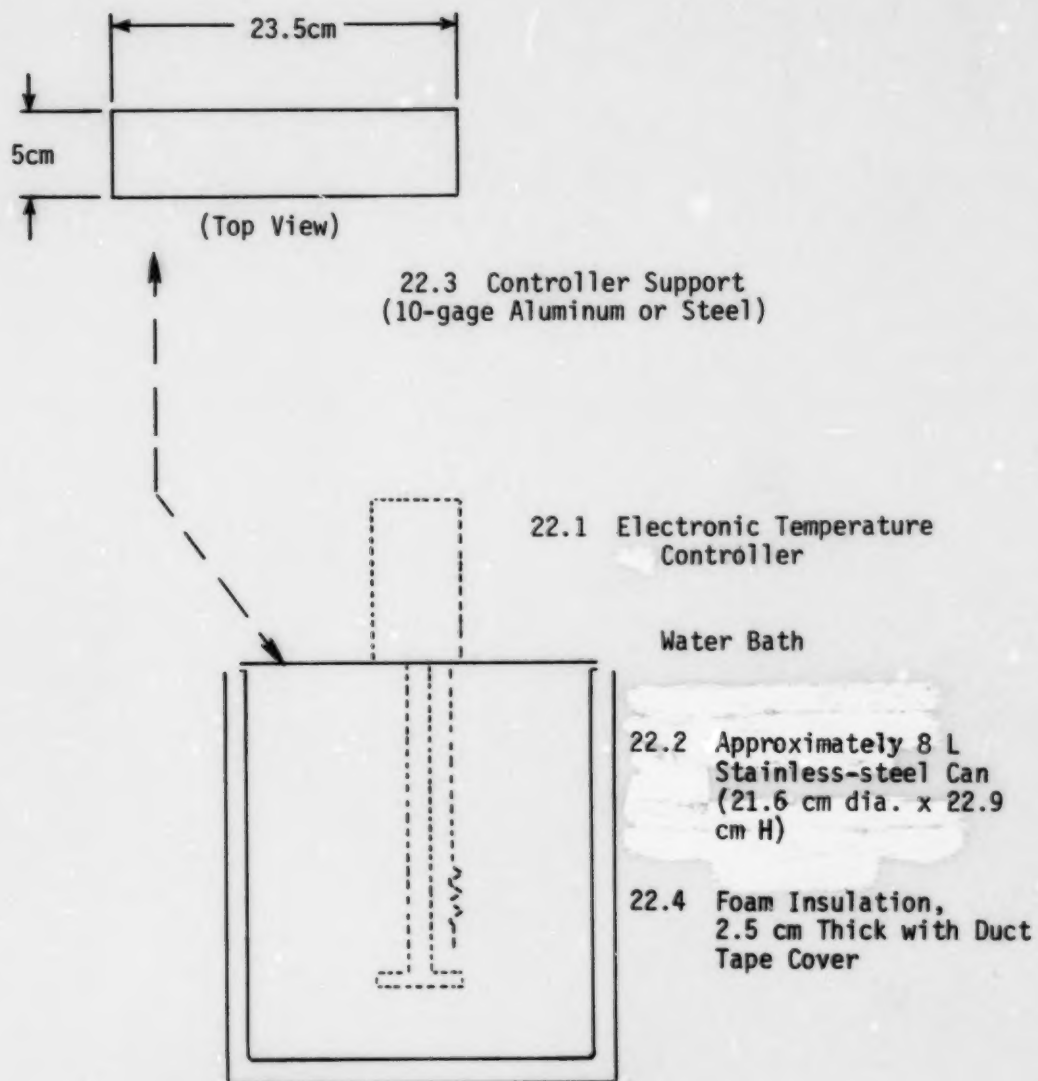


Figure 22. Circulating hot-water-bath assembly.

SUPPORT EQUIPMENT

Peripheral equipment used with the MACS system is individually listed below.

Parts and Materials Specifications (Support Equipment)

Pyrometer (Part No. 23.1):	Digital pyrometer with K-type thermocouple calibration, 40°C to 1000°C. range, with miniature quick-connect termination.
Timer (Part No. 23.2):	Stopwatch type with 0.1-sec resolution.
Port Cap (Figure 23):	Black pipe cap, 10.16 cm (4 in.) with 2.54 cm (1 in.) Ultra-Torr Adapter welded in place.
Support Bracket (Figure 24):	1.3-cm steel angle (1 mL) with attached bracket for mounting to port cap.
Leak-check Drying Tube (Figure 25):	Drying tube with 12/5 ball, tubing and pinch clamp for filter-holder inlet. Also requires a closed-end 12/5 socket for probe (not shown in Figure 25).

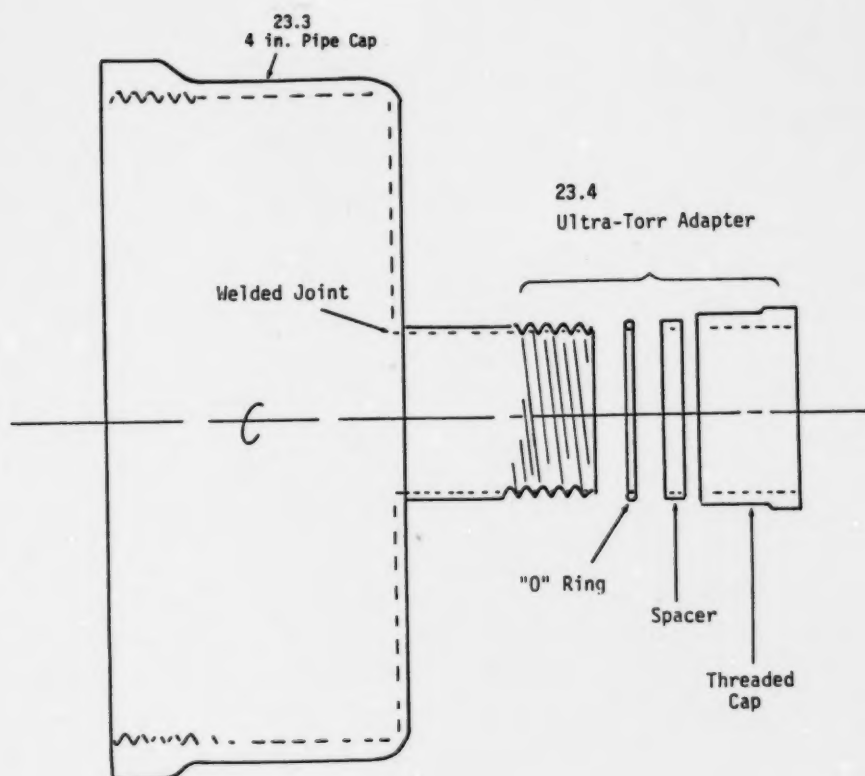


Figure 23. Port-cap assembly.

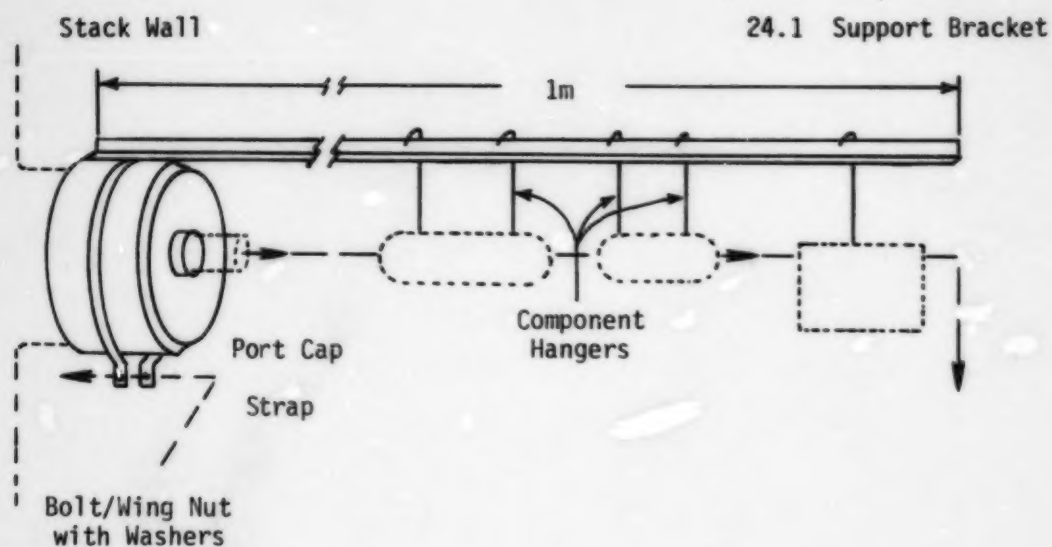


Figure 24. Sampling-train support bracket.

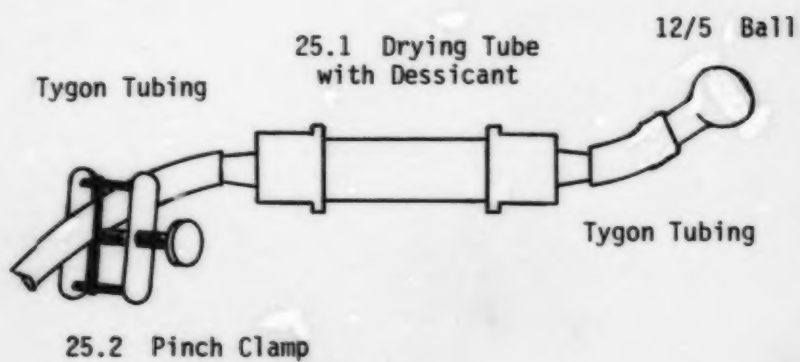


Figure 25. Leak-check drying tube.

SECTION 5

PARTS/MATERIALS LIST, FABRICATION COSTS

This section contains a complete listing of parts and materials required to assemble the MACS system. Since this sampling system is not currently available from commercial sources as a completely assembled unit and, therefore, must be user-fabricated, one may reasonably expect substitution and/or modification of parts and materials. The parts and materials described in Section 4 and listed in this section are provided as a guide for fabricating a functional system.

The identification of specific vendors for certain parts does not constitute an endorsement of the vendors mentioned nor does it reflect the nonavailability of these parts from other sources.

The costs shown in the parts listing for parts and materials are based on current catalog prices or vendor quotations. Labor costs incurred for construction of prototype parts either by a subcontractor or the user are based on an arbitrary rate of \$30/h.

PARTS/MATERIALS LIST

The parts and materials listed in Table 1 are keyed with a reference number to the figures shown in Section 4. One or more suggested suppliers are given for commercially-available parts and where applicable, local vendors are suggested for materials or parts to be fabricated.

TABLE 1. PARTS/MATERIALS LIST

<u>Component</u>				
Reference Number	Part/Material	Description	Suggested Supplier(s)	Estimated Cost (dollars)
<u>Sample Probe</u>				
9-1, 9-5,	K-type thermocouple	Chromel alumel alloys, felted asbestos insulation (2 cm L)	Omega Engineering, Inc.	4.50
9-2, 9-6	Sample tube	Quartz tube with 12/5 ground glass ball joint and thermowell.	Scientific glass shop, local	85.00*
9-3	Sheath	Thin-wall, 304 stainless steel, 25 mm O.D. sheath.	Industrial supplier, local	5.50
9-4, 9-7	Heat tape	1.3 cm x 18.3 cm, 288 W, with two-piece connector	Fisher Scientific	15.50
9-8, 9-9	K-type thermocouple connector	Chromel alumel, miniature male connector.	Omega Engineering, Inc.	5.00
<u>Quartz-Filter Holder</u>				
10-1, 11-1	Quartz-filter holder	Quartz 28/15 ground glass joint with coarse-quartz-frit filter and with quartz 12/5 ground glass interface joints	Scientific glass shop, local	130.00*
11-2	K-type thermocouple	Chromel alumel alloys, felted asbestos insulation (25 cm L).	Omega Engineering, Inc.	.50
11-3	K-type thermocouple connector	Chromel alumel, miniature male connector	Omega Engineering, Inc.	2.50
12-1	Tubular heating jacket	Jacket-type, 150 mm L x 150 mm thick, 115 VAC, 175 W with two-prong male connector.	Brisco Manufacturing Co.	90.00

* Estimated cost includes parts and labor.

TABLE 1. PARTS/MATERIALS LIST
(continued)

<u>Component</u>				
Reference Number	Part/Material	Description	Suggested Supplier(s)	Estimated Cost (dollars)
<u>Glass-plug Holder</u>				
13-1	Glass-plug holder	Typical condenser-type construction with a 4-mm tube mounted inside a 30-mm tube and with 12/5 ground glass joints. Fabricated with Pyrex® glass.	Scientific glass shop, local	40.00*
13-2	Reducing connector	Pyrex® glass elbow with 12/5 ground glass socket to an 18/9 ground glass socket.	Scientific glass shop, local	25.00*
13-3	Insulating tape	Thermal-aluminum face/adhesive back duct tape.	Local hardware	5.00
<u>Impinger Train and Ice Bath</u>				
14-1	Midget impinger	30 ml graduated, with 24/40 stopper/bottle joint and 18/9 ground glass ball stopper joints (4 assemblies required).	ACE Glass	80.00
14-2	U-tube connector	U-tube with 18/9 ground glass sockets (three pieces required).	Scientific glass shop, local	25.00*
14-3	Impinger/pump connector	12-mm heavy wall Pyrex® tube with 18/9 glass socket.	Scientific glass shop, local	15.00*
14-4	Pressure fitting	Swagelok stainless-steel reducer, 12-mm tube to 12.7-mm male tube.	Crawford Fitting Company	15.00
14-5	Quick-connect	Swagelok stainless-steel, 12.7-mm tube pressure fitting, double end shut off stem assembly.	Crawford Fitting Company	30.00

* Estimated cost includes parts and labor.

TABLE 1. PARTS/MATERIALS LIST
(continued)

Component Reference Number	Part/Material	Description	Suggested Supplier(s)	Estimated Cost (dollars)
15-1	Aluminum can	16-gage aluminum can (100mm W x 200mm L x 150mm H), with 25-mm lip welded seams.	Sheet metal shop, local	25.00*
15-2	Impinger support	10-gage aluminum plate (50 mm W x 200 mm L).	Sheet metal shop, local	5.00
15-3	Support arm	16-gage aluminum plate (25 mm W x 125 mm L), with right angle bend at 25 mm.	Sheet metal shop, local	5.00
15-4	Insulating foam	Polystyrene (or equivalent) foam, 14 cm ² .	Local builder's supply	8.00
15-5	Insulating covering	Heat duct tape.	Local builder's supply	10.00
<u>Sample Pump/ Metering Unit</u>				
16-1	Quick-connect	Double end shut off, bulkhead, 6.35 mm pressure fit tube connection, stainless steel.	Parker Hannifin	15.00
16-2, 16-3	Bulkhead adapter	6.35 mm tube connection, stain- less steel.	Parker Hannifin	8.00
16-4, 16-5 16-8	Elbow (M)	6.25 mm tube connection to 9.53 mm NPT, stainless steel.	Parker Hannifin	15.00
16-6, 16-7	Connector (M)	6.25 mm tube to 3.18 mm NPT, stainless steel.	Parker Hannifin	8.00
16-9	Reducing bushing (two required)	12.7 mm (M) NPT to 6.25 mm (F) NPT, stainless steel.	Parker Hannifin	8.00

* Estimated cost includes parts and labor.

TABLE 1. PARTS/MATERIALS LIST
(continued)

<u>Component</u>				
Reference Number	Part/Material	Description	Suggested Supplier(s)	Estimated Cost (dollars)
16-10	Branch tee (M)	6.25 mm tube to 6.25 mm (M) NPT, stainless steel.	Parker Hannifin	6.00
16-11	K-type thermocouple	Chromel alumel alloys, felted asbestos insulation (2 cm L).	Omega Engineering, Inc.	1.25
16-12	Thermocouple connector	Miniature, chromel alumel (K-type), panel mount.	Omega Engineering, Inc.	3.00
16-13	Drying tube	Polyethylene (18 cm L) with end caps (Figure 20).	Fisher Scientific	--
16-14	Rotameter	0.5 l to 5 l/min, panel mount with metering valve.	Dwyer Controls and Gage	75.00
16-15	Sample pump	Teflon® diaphragm type, 50 cm Hg vacuum, 3 l/min capacity, 115 VAC.	Cole-Parmer Instrument Company	120.00
16-16	Power connector	Two (2) conductor with ground, recessed (M) panel mtg 115 VAC, 6 amp minimum rating.	Electrical Distributor, local	1.50
16-17	Fuse holder/fuse	Holder: Standard panel mtg for 3AG-type fuse, Fuse: 3 AG type with 2 amp rating.	Electrical Distributor, local	2.00
16-18	Switch	Toggle-type, SPST, panel mount, 125 VAC, 3 amp rating.	Electrical Distributor, local	2.20
16-19	Dry-gas test meter	Domestic gas-meter type, 6 M/hr capacity.	Rockwell International	74.00
17-1	Dry test meter/pump housing	Schedule 90 aluminum with welded seam construction (Figure 17).	Sheet metal shop, local	80.00
17-2	Hinge	Piano type, 40 cm L.	Local hardware	1.70

TABLE 1. PARTS/MATERIALS LIST
(continued)

<u>Component</u>				
Reference Number	Part/Material	Description	Suggested Supplier(s)	Estimated Cost (dollars)
17-3	Handles (two)	Draw-pull type.	Local hardware	3.40
18-1	Tubing connectors (two)	Quick-connect type (M), 12.7 mm tube.	Parker Hannifin	15.00
18-2	Tubing	Heavy Wall Tygon, 12 mm O.D. x 6 m L.	Fisher Scientific	1.00
20-1	Drying tube	Polyethylene (18 cm L) with end caps.	Fisher Scientific	7.25
20-2	Bulkhead adapter	6.35 mm tube connection, stainless steel (two pieces required).	Parker Hannifin	8.00
<u>Temperature Controls</u>				
21-1	Controller	Proportional type for K-type thermocouple sensing, Electronic indicating, manual set point, 0°F - 600°F range (two units required).	Omega Engineering, Inc.	430.00
21-2	Controller cabinet	Shadow cabinet (39.4 cm W x 22.9 cm L x 15.2 cm H).	Newark Electronics	25.00
21-3	Thermocouple connector	Steel or aluminum construction miniature K-type inline (F) (two required).	Omega Engineering, Inc.	5.00
21-4	Power connectors	Two (2) conductor (F) inline AC connectors (two required).	Electrical distributor, local	3.00
21-5	Power connector	Two (2) conductor with ground (M), molded type with 2 m cord, 115 VAC, 10 amp capacity, 600 V insulation.	Electrical distributor, local	8.00
21-6	Fuse holder/fuse	Standard panel mount for 15 amp, 3 AG-type fuse.	Electrical distributor, local	2.00

TABLE 1. PARTS/MATERIALS LIST
(continued)

<u>Component</u>				
Reference Number	Part/Material	Description	Suggested Supplier(s)	Estimated Cost (dollars)
22-1	Circulator/temperature controller	Constant-temperature immersion circulator type, 30°C to 100°C range, + 0.03°C accuracy complete with thermoregulator.	Cole Parmer Instrument Company	530.00
22-2	Water bath	Stainless-steel can, 8-l capacity (approximately 22 cm dia. x 23 cm H).	Fisher Scientific	41.00
22-3	Circulator support	10-gage aluminum plate (23.5 cm L x 5 cm W) or to fit part 22.2.	Sheet metal shop, local	10.00
22-4	Insulation	Polystyrene (or equivalent) foam, 14 cm ² (1 m ²).	Builder's supply, local	4.00
<u>Support Equipment</u>				
23-1	Pyrometer	Digital or dial type with K-type thermocouple calibration, 40°C to 1000°C. range, with miniature quick-connect termination.	Cole Parmer Instruments Company	186.00
23-2	Timer	Stopwatch type with minimum 0.1 sec resolution.	Fisher Scientific; Cole Parmer Instrument Company	50.00
23-3	Port cap	Black pipe cap, 10.2 cm (4 in.).	Local hardware	8.00
23-4	Adapter	Ultra-Torr Adapter, 25.4 I.D., stainless steel, with O-ring seal.	Parker Hannifin	65.00
24-1	Support bracket	Angle-steel stock, 16-gage, (1.3 cm x 1.3 cm x 1 m) with 16-gage steel strap, (1.3 cm W x 35 cm L).	Sheet metal shop, local	6.00
24-2	Clamp	Hoffman-Pichcock type, 10 mm to 20 mm opening.	Fisher Scientific	1.25
25-1	Drying tube	Polyethylene (18 cm L) with end caps.	Fisher Scientific	7.25

FABRICATION COSTS (Dollars)

Sample Probe

Parts and Materials.	115.50	
Labor.	720.00	
		<u>Subtotal 835.50</u>

Quartz-filter Holder

Parts and Materials.	223.00	
Labor.	---	
		<u>Subtotal 223.00</u>

Glass-plug Holder

Parts and Materials.	70.00	
Labor.	---	
		<u>Subtotal 70.00</u>

Impinger Train and Ice Bath

Parts and Materials.	218.00	
Labor.	120.00	
		<u>Subtotal 338.00</u>

Sample Pump/Metering Unit

Parts and Materials.	455.30	
Labor.	1200.00	
		<u>Subtotal 1655.30</u>

Temperature Controls

Parts and Materials.	1058.00	
Labor.	720.00	
		<u>Subtotal 1778.00</u>

Support Equipment

Parts and Materials.	323.50	
Labor.	240.00	
		<u>Subtotal 563.50</u>

Other Labor Costs

Parts and Materials Acquisition and Inspection	1200.00	
Component and System Check(s).	1000.00	
		<u>Subtotal 2200.00</u>

TOTAL COST	<u>7663.30</u>
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APPENDIX A

BARIUM THORIN DETERMINATION OF SO_4 ION

Thorin Indicator. 1-(o-arsonophenylazo)-2-napthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

Barium-Perchlorate Solution. 0.0100 N. Dissolve 1.95 g of barium perchlorate tri-hydrate $[\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}]$ in 200 ml distilled water and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of $[\text{BaCl}_2 \cdot 2\text{H}_2\text{O}]$ may be used instead of the perchlorate. Standardize using the H_2SO_4 Standard 0.0100 N solution.

H_2SO_4 Standard. 0.0100 N. Purchase or standardize to ± 0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

CALCULATIONS

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

Nomenclature.

- C_{SO_2} = Concentration of SO_2 , dry basis corrected to standard conditions, mg/dscm.
- N = Normality of barium perchlorate titrant, milliequivalents/ml.
- P_{bar} = Barometric pressure at the exit orifice of the dry-gas meter
- P_{std} = Standard absolute pressure, 760 mm Hg
- T_{m} = Average dry-gas-meter absolute temperature
- T_{std} = Standard absolute temperature, 293°K.

- V_a = Volume of sample aliquot titrated, ml.
 V_m = Dry-gas volume as measured by the dry-gas meter, dcm.
 $V_{m(std)}$ = Dry-gas volume measured by the dry-gas meter, corrected to standard conditions, dscm.
 V_{soln} = Total volume of solution in which the SO_2 is contained, 100 ml.
 V_t = Volume of barium perchlorate titrant used for the sample, ml (average or replicate titrations).
 V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.
 Y = Dry-gas meter calibration factor.

To correct the sample-gas volume to reference standard conditions:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} = K_1 Y \frac{V_m P_{bar}}{T_m}$$

where $K_1 = 0.3858^\circ K/mm \text{ Hg}$ for metric units.

To calculate SO_2 concentration in mg/dscm:

$$C_{SO_2} = K_2 \frac{(V_t - V_{tb}) N (V_{soln}/V_a)}{V_{m(std)}}$$

where $K_2 = 32.03 \text{ mg/meq}$ for metric units.

For calculations involving SO_4 ions, including H_2SO_4 and metal sulfates, the calculations are the same except $K_2 = 48.04 \text{ mg/meq}$.

Titration of the peroxide catch of SO_2 as SO_4 using the barium-thorin procedure is simple and straightforward. Using the same procedure to quantify the SO_4 in the filter and filter-holder washes, as well as the probe washes can involve some analytical difficulties. The presence of metal ions in these fractions can mask the colorimetric endpoint by either affecting the pH of the solution or by reacting with the thorin indicator. To avoid such difficulties, remove the metal ions by passing the aliquot to be analyzed through a cation-exchange resin. During passage, the metal

ions are removed and replaced with hydrogen ions, which result in a lower pH. At this lower pH (5.0 or less), the sensitivity and selectivity of the barium-thorin complex is optimum, with a clear yellow to pink color transition at the endpoint.

If the probe and filter fractions are recovered by the alternate method to distinguish metal sulfates from H_2SO_4 and $[\text{NH}_4]_2\text{SO}_4$, the 100% isopropanol wash must be diluted below 80% IPA to protect the column.

Prepare the column by soaking approximately 20 ml of a sulfonated organic polymer cationic type resin in 80% isopropanol. (e.g., Rexyn 101 (H) a strong acid cation exchange resin can be obtained from Fisher Scientific).

Insert into a 25 ml buret a small glass-wool plug and push down to the bottom just above the stopcock. Transfer the resin and the solution, after soaking for 24 h to the buret. Allow the isopropanol to drain out of the buret as the solution is added until the resin builds up to the 12 ml mark. Insert another small glass-wool plug into the buret and push down until it rests on top of the resin bed. The column should now be rinsed several times with reagent 80% isopropanol. Bubbles which accumulate within the resin-bed column minimize solution contact and therefore, should be removed frequently. This may be done easily by pulling the solvent up through the bottom of the buret, with the stopcock open and a vacuum applied to the top of the buret. The resin should never be allowed to dry, and the solvent should be replaced with fresh reagent solvent any time the column is not used for 24 h or more.

To use the column, add a 10 ml aliquot of the sample to the buret and allow it to pass through the resin bed and into the titration flask at a rate of one ml/min. Following the sample aliquot with four-10 ml additions of 80% isopropanol produces a total of 50 ml of an 80% isopropanol solution in the titration flask. The indicator can be added and the 50 ml titrated with the barium solution.

The ion-exchange resins are usually some type of sulfonated organic polymers which, upon any degradation, will result in the formation of SO_4 ions. Therefore, prior to using the column each day, perform a blank on

the resin-bed solvent by passing 50 ml of solvent through the bed and make a SO_4 determination on the rinse.

Accumulated metals in the bed can be removed by washing the bed with 6 N HNO_3 . A blank should always be performed following the nitric acid rinse to remove the metals.

APPENDIX B

IC DETERMINATION OF SO_3^- AND SO_4^-

REAGENTS

Eluent. 0.0005 M NaHCO_3 /0.0035 M Na_2CO_3 . Dissolve 0.168 g NaHCO_3 and 1.48 g Na_2CO_3 in 4.0 L of deionized water.

I.C. Calibration Standard Stock Solutions.

Stock formalin Solution (10% μ/v): Dilute 100 ml of Certified American Chemical Society Formalin solution (37% W/V) (Fisher Scientific) to 1000 ml with deionized water.

Stock SO_3^- Standard Solution (100 $\mu\text{g}/\text{ml}$ in 0.1% formalin solution): Pipet 10 ml of 10% formalin solution into a 1.0 L volumetric flask containing approximately 750 ml of deionized water and mix thoroughly. Dissolve 0.1574 g dried, Certified American Chemical Society reagent grade Na_2SO_3 in the solution and dilute to the mark with deionized water.

Stock Nitrate (NO_3^-) Standard Solution (100 $\mu\text{g}/\text{ml}$ in deionized water): Dissolve 0.13708 g dried, Certified American Chemical Society reagent grade NaNO_3 in 1.0 L of deionized water.

Stock SO_4^- Standard Solution (100 $\mu\text{g}/\text{ml}$ in deionized water): Dissolve 0.18140 g dried, Certified American Chemical Society reagent grade K_2SO_4 in 1.0 L of deionized water.

IC Calibration Standard Solutions.

Mixed Standard for Use on 10 μmho range: (2.0 $\mu\text{g}/\text{ml}$ SO_3^- , 1.0 $\mu\text{g}/\text{ml}$ NO_3^- , 5.0 $\mu\text{g}/\text{ml}$ SO_4^- in 0.1% formalin solution). Pipet 10 ml of 10% formalin solution into a 1.0 L volumetric flask containing approximately 750 ml of deionized water and mix thoroughly. Pipet 20 ml of the stock (100 $\mu\text{g}/\text{ml}$) SO_3^- standard

solution, 10 ml of the stock NO_3^- standard solution, and 50 ml of the stock SO_4^{2-} standard solution into the flask and dilute to the mark with deionized water.

GENERAL ANALYSIS PROCEDURE

Since SO_3^{2-} ion is generally present in significant amounts in some of the MACS sample train fractions, and NO_3^- is also usually present, the procedure described here was developed to achieve maximum separation of the three species (SO_3^{2-} , NO_3^- , and SO_4^{2-}) thereby minimizing the possible interferences in a routine analysis for SO_4^{2-} . The use of dilute formalin solutions for standards containing SO_3^{2-} ion yields a stable solution with a shelf life of approximately 12 mo.

The method requires the use of three analytical separator columns in series as follows: a 3x50 mm guard column, a 3x250 mm separator column, and a 3x500 mm separator column. A 6x250 mm suppressor column is should be used. Pump the eluent (0.0005 M HCO_3^- /0.0035 M CO_3^{2-}) at 35% of the maximum flow rate. The retention times for the various species in the standard solution under these conditions are 7.3, 9.8, and 12.4 min for SO_3^{2-} , NO_3^- , and SO_4^{2-} ions, respectively. SO_4^{2-} is completely eluted from the column in 15 to 16 min. Peak quantitation is generally achieved using area integration; however, the measurement of peak heights can also be used. For most applications, samples contain sufficient amounts of sought-for species to allow use of the 10 μmho range of the instrument when a 50 μL sample loop is employed. Table B-1 shows a summary of column conditions, standards, and dilution procedures for SO_4^{2-} analysis of the MAC's sample fractions.

SAMPLE-PREPARATION PROCEDURE

In general, MACS sample fractions received for analysis are recovered quantitatively from their sample containers by filtering through prewashed Whatman No. 541 filter paper into volumetric flasks followed by dilution to

TABLE B-1. ION CHROMATOGRAPHIC REQUIREMENTS FOR SULFATE ANALYSIS

Sample Fraction	Range of Concentration (Total Mg. SO_4)	Sample Dilution Volume (ml)	IC Standard ($\mu\text{g/ml}$)	IC Conditions
Comb. PW, Filter, Filter Holder	0.36-0.93	100-200	2.0 SO_3 , 1.0 NO_3 , 5.0 SO_4	10 μmho range 500 μL loop
Plug Wash	0.15-0.44	100	"	"
H_2O_2 IMP Catch	21.8-50.6	250	100.0 SO_4	30.0 μmho range 50 μL loop

a known volume using 80% IPA/20% H₂O. The filters are prepared for analysis by extraction in 20 ml of deionized water using ultrasonic bath for a period of 30 min. The extraction solution is then quantitatively recovered according to the procedure as utilized for the other fractions. Details of the recovery procedure are described in the following paragraph.

Fold a Whatman No. 541 filter and place in a pyrex funnel (long stemmed) and rinse with three successive volumes of deionized water. Then place an appropriate sized volumetric flask under the funnel and filter the sample into the flask. Rinse the sample container three times with deionized water (approximately 10-30 ml each, depending on total sample volume), pouring each rinse through the funnel. After the final rinse, remove the filter paper and rinse the funnel into the sample. Then dilute the flask to the mark.

To avoid damage to the analytical columns of the IC, dilute samples containing isopropanol such that the sample for analysis contains no greater than 25% (by volume) isopropanol. Similarly, samples containing H₂O₂ should be diluted so that the sample for analysis contains no greater than 0.6% H₂O₂ (by volume).

PROCEDURES FOR EXTRACTION AND ANALYSIS OF SAMPLE USING 100% IPA

In experiments designed to remove free H₂SO₄ from filters for separate IC analysis, the following procedure can be employed: using an appropriate size Buchner funnel and filtering flask with vacuum applied, rinse the filter with a volume of isopropanol (100%) equal to 25% of the total sample-dilution volume. (For a MACS sample-train filter (16 mm) a dilution volume of 100 ml is typical, and would require a rinse of 25 ml of 100% IPA.) Then quantitatively recover the filtrate using deionized water. The filter can then be extracted by ultrasonication in the normal manner using deionized water.

APPENDIX C

RESULTS OF SAMPLING WITH THE MACS SYSTEMS

This Appendix compares data acquired with the larger Acid Condensation System (ACS) and the smaller Micro-Acid Condensation System (MACS). An oil-fired boiler was sampled with an ACS and a MACS system, and a coal-fired boiler with two MACS systems. The ACS system has a 47 mm quartz filter and samples at a nominal 10 l/min, and the MACS system has a 16 mm quartz filter and samples at a nominal 1.0 l/min. Both systems have quartz probes. Filter temperatures are maintained at or above 520°F during sampling. The ACS collects the SO₂ in Greenberg-Smith type impingers with 3% hydrogen peroxide (H₂O₂); the MACS collects SO₂ in midjet impingers with 3% H₂O₂.

Table C-1 shows the results of sampling at the oil-fired boiler. The particulate sulfate (P-SO₄) results include both the sulfate recovered from the probe wash (PW) and the quartz filter and filter holder (F). The total sulfate (Σ) collected by each system includes the sulfuric acid (H₂SO₄) recovered from the glass wool plug (GP) and the total particulate sulfate (P-SO₄). The percent of the total sulfate (Σ) collected in the glass plug (GP) represents the percent of the sulfate in the emissions as H₂SO₄. For these data, an average of 76.3% of the total sulfate was H₂SO₄ using the ACS results. The MACS system results show that 55.0% of the sulfate was H₂SO₄. This indicates that at the 1.0 l/min sampling rate, some of the H₂SO₄ is being retained in the probe and on the filter. The total sulfate and SO₂ show good agreement when averaging the two sampling system results. The percent standard deviations (STD) are 9.04% and 6.08% for the total sulfate and SO₂, respectively.

Different sampling rates were sometimes used when sampling the coal-fired boiler using identical MACS systems. The results of the sampling train analyses are shown in Table C-2. The results in Table C-2 are presented in terms of moles of sulfur included in sulfates as a fraction of moles of sulfur that was included as SO_2 in the peroxide impinger. The STD for the total sulfate ($\text{T-SO}_4^{=}$) collected by the two MACS is 10.0% for all 8 paired runs. For the first 3 pairs of runs which involved nearly identical sampling rates, the total sulfate STD is 7.8%. The variation in percent H_2SO_4 for these first 3 runs is 3.0. For the last 5 paired runs, where the sampling rate was kept near a 3 to 1 ratio, the STD for total sulfate is 11.3%. The variation in percent H_2SO_4 for these 5 runs is 4.7. The final column in Table C-2 identifies the fraction (as percent Sulfur) of the total sulfur oxides collected that were primary sulfate sulfur.

When sampling any type of source emission where H_2SO_4 can interact with particulate matter, a more effective H_2SO_4 determination can be made by recovering the probe and filter using 100% isopropanol (IPA). The 100% IPA will solubilize the H_2SO_4 but not the metallic sulfates and will hence separate them. A subsequent washing of the probe and filter with H_2O will still provide a total sulfate estimate.

TABLE C-1. RESULTS OF SAMPLING AN INDUSTRIAL OIL-FIRED BOILER

Run No.	Sampling System	Mg SO ₄ /M ³					Mg SO ₂ /M ³			
		PW	F	P-SO ₄ ^(a)	GP	Σ ^(b)	Avg.	STD	H ₂ O ₂	STD
1	ACS MACS	13.19 38.05	16.28 25.60	29.47 63.65	64.71 55.84	94.18 119.50	106.81 ± 11.8		1373 1713	1544 ± 11.0
2	ACS MACS	4.76 19.21	10.74 17.38	15.50 36.59	61.90 50.88	77.40 87.47	82.44 ± 6.11		996 1373	1185 ± 15.9
3	ACS MACS	11.31 37.93	14.33 38.94	25.64 76.87	92.51 65.08	118.15 141.95	130.1 ± 9.15		1642 1805	1724 ± 4.73
4	ACS MACS	13.76 24.34	26.62 15.34	40.38 39.68	77.33 84.66	117.71 124.34	121.0 ± 2.74		1338. 1569	1454 ± 7.94
5	ACS MACS	4.15 35.41	14.20 27.84	18.35 63.25	85.06 42.08	103.41 105.33	104.4 ± 0.92		1479 1474	1477 ± 0.20
6	ACS MACS	15.18 13.80	13.06 16.84	28.24 30.64	51.40 56.70	79.64 87.34	83.4 ± 4.61		1194 1219	1207 ± 1.04
7	ACS MACS	3.34 31.71	12.86 22.59	16.20 54.30	86.69 97.19	102.89 151.49	127.2 ± 19.1		1417 1561	1489 ± 4.84
8	ACS MACS	10.22 28.82	14.49 18.80	24.71 47.62	94.63 54.86	119.34 102.48	110.9 ± 7.60		1721 1685	1703 ± 1.06
9	ACS MACS	8.26 38.34	11.19 29.43	19.45 67.77	91.94 115.47	111.39 183.24	147.3 ± 24.4		1664 2006	1835 ± 9.32
10	ACS MACS	8.18 20.02	7.90 17.38	16.08 37.40	54.74 45.18	70.82 82.58	76.7 ± 7.67		1020 1099	1060 ± 3.73
11	ACS MACS	17.94 46.89	15.95 31.54	33.89 78.43	110.00 75.17	143.89 153.60	148.7 ± 3.26		1770 1495	1633 ± 8.42
12	ACS MACS	16.48 42.33	15.47 38.58	31.95 80.91	103.99 89.42	135.94 170.33	153.1 ± 11.23		1647 1813	1730 ± 4.80

(a) P-SO₄ = Probe SO₄ + Filter SO₄(b) Σ = Probe SO₄ + Filter SO₄ + Glass Plug H₂SO₄

Average STD for Total Sulfate is ± 9.04%

Average STD for Sulfur Dioxide is ± 6.08%

TABLE C-2. RESULTS OF SAMPLING A UTILITY COAL-FIRED BOILER

Run No.	Sampling System	Sampling Rate (l/m)	μ moles sulfate-S/mm SO_2 -S(a)						STD	$\% \text{H}_2\text{SO}_4$ (d)	$\% \text{C(e)}$
			PW	F	P-SO ₄ (b)	GP	T-SO ₄ (c)	Avg.			
1	MAC-1 MAC-2	2.7 3.2	.772 .072	1.056 1.300	1.828 1.372	1.749 1.312	3.577 2.684	3.13 ± 0.44		48.9 48.9	0.36 0.27
2	MAC-1 MAC-2	2.6 2.8	.109 .078	1.654 1.244	1.763 1.323	1.763 1.711	3.526 3.034	3.28 ± 0.24		50.0 56.4	0.35 0.30
3	MAC-1 MAC-2	2.7 3.0	.098 .080	1.436 1.155	1.534 1.236	3.183 3.297	4.717 4.533	4.63 ± 0.09		67.4 72.7	0.47 0.45
4	MAC-1 MAC-2	0.8 2.8	.324 .053	.910 .507	1.234 .560	1.616 1.416	2.850 1.976	2.41 ± 0.44		56.7 71.7	0.33 0.20
5	MAC-1 MAC-2	0.9 2.9	.140 .053	1.907 1.409	2.047 1.462	1.449 1.346	3.496 2.808	3.15 ± 0.34		41.4 47.9	0.35 0.28
6	MAC-1 MAC-2	0.9 3.0	.331 .249	1.173 .784	1.504 1.034	5.423 3.868	6.927 4.902	5.91 ± 1.01		78.3 78.9	1.59 1.49
7	MAC-1 MAC-2	0.9 3.0	.338 .160	1.041 .752	1.379 .912	5.967 5.662	7.346 6.574	6.96 ± 0.39		81.2 86.1	0.73 0.66
8	MAC-1 MAC-2	0.9 3.0	.338 .500	1.121 .656	1.459 1.156	5.338 5.004	6.797 6.160	6.48 ± 0.32		78.5 81.2	0.68 0.62

(a) μ moles sulfate-sulfur/mm SO_2 -S calculated as: $(\mu\text{g SO}_4 / 96 \mu\text{g SO}_4 / \mu\text{m SO}_4 - \text{S}) / (\text{mg of SO}_2\text{-S}/64 \text{ mg of SO}_2\text{-S/mm SO}_2\text{-S})$ (b) P-SO₄ = Probe sulfate + filter and filter holder sulfate(c) T-SO₄ = P-SO₄ + H₂SO₄ in glass plug(d) $\% \text{H}_2\text{SO}_4$ = Glass plug (GP)/T-SO₄ (X 100%)(e) (Sulfate-S)/(Sulfate-S + SO₂-S) X 100%